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YIELD AND PURITY OF LEVULOSE DERIVED FROM THE CALCIUM LEVULATE PROCESS

By Richard F. Jackson and Joseph A. Mathews

ABSTRACT

Calcium levulate, although relatively insoluble in water, is appreciably soluble in sugar solutions. The yield of levulose from sugar mixtures is therefore dependent upon the ratio of levulose to total sugar in the crude mixture. The principal nonlevulose sugars occurring in plant juices after hydrolysis of the polysaccharides are dextrose and the isomeric difructose anhydrides. As a by-product of hydrolysis fructosans may be introduced. Data are given which show how much levulate is held in solution by dextrose and by the difructose anhydrides. Increased temperature diminishes the yield of levulate markedly. Quantitative measurements were made which show the yield of levulate from various crude juices and the distribution of levulose, total reducing sugar, and lime among the waste water, wash, and levulate cake. The data show satisfactory product balances.

The levulate cake suspended in water and decomposed with carbon dioxide yielded sirups of purities fluctuating between 91 and 97 percent. It was ascertained that the sugar suffered a loss of purity during the transformation of calcium bicarbonate to carbonate, which imparted an alkaline reaction to the solution. In the final series of experiments calcium bicarbonate was removed from the cold suspension by additions of lime. From the resulting filtrate calcium was precipitated quantitatively by oxalic acid. All adjustments were made by means of conductometric measurement. By the modified method levulose sirups of 99 percent purity were obtained.

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I. INTRODUCTION

In a previous article Jackson, Silsbee, and Proffitt [1] described a process for the preparation of levulose from the juices of the jerusalem artichoke and other natural sources in which the levulose was isolated from the crude juice, after hydrolysis of the polysaccharides, by means of a modification of Dubrunfaut's calcium levulate method, the modification producing a readily filterable suspension instead of the difficultly filterable mixture of the original process. The levulose sirups obtained in a number of experiments showed purities which averaged 93.8 percent, but which fluctuated without explainable cause over the wide range from 91 to 97 percent. The predic-

[1] BS Sci. Pap. 20, 587 (1926), S519.

tion was made [2] that "there are still some undetermined factors which upon further study will tend to produce the higher purities and yields more uniformly." In the present investigation we have sought to discover the influences which affect the yield of levulate, and particularly to modify the procedure in order to obtain higher purities in the final levulose sirups.

II. PRECIPITATION OF CALCIUM LEVULATE

In the article cited it was shown that calcium levulate could be caused to precipitate in a coarsely crystalline state, which permitted rapid filtration and washing, by making continuous additions of lime and levulose to a suspension of previously formed levulate, the newly formed levulate tending to deposit on nuclei already present, building them up in some instances to a length of 0.2 mm, and increasing their cross section correspondingly. This method was followed in the experimental work described in the present paper.

In applying the method to the miscellaneous materials from which levulose could be prepared it was observed that the yield of levulate was, as in the previous work, subject to wide fluctuations. In the earlier article it was shown that the solubility of calcium levulate was increased by dissolved dextrose or by an excess of levulose. Experiment showed that the precipitate was also soluble in sucrose solutions. It then appeared probable that calcium levulate was more or less dissolved by any sugar which occurred in the product serving as the source of levulose and that the presence of nonlevulose sugars was mainly responsible for the fluctuating yields.

The problem then was to identify the nonlevulose sugars which occurred in the juices and to measure their effect on the solubility of calcium levulate. The present discussion is concerned particularly with artificial mixtures of pure sugars and with the juices of the jerusalem artichoke, dahlia, and chicory. It will be assumed that the polysaccharides in the plant juices have been hydrolyzed, preferably by sulphuric acid, and the juices defecated after cooling to room temperature by addition of milk of lime to pH 7 to 8.

The principal nonlevulose sugars which occur in such plant juices are dextrose, which invariably accompanies levulose in natural products, and the three isomeric difructose anhydrides [3] which are always present in the products of the acid hydrolysis of inulin. Conceivably other sugars may occur, but probably in small amount.

In addition to the sugars mentioned, whose presence is unavoidable, others may be present which are introduced during hydrolysis and defecation. If the hydrolysis reaction is prolonged levulose suffers the loss of 1 molecule of water and changes to the nonreducing fructosans first isolated by Pictet and Chavan,[4] and designated by them heterolevulosan and its dimer, diheterolevulosan. Mathews and Jackson [5] have shown that this dehydration occurs not only in the extreme acidity employed by Pictet and Chavan, but in the more mildly acid solutions required for the hydrolysis of inulin. These fructosans are therefore present in all juices in which the polysaccha-

[2] See p. 612 of reference 1.
[3] Jackson and Goergen, BS J. Research **3**, 27 (1929) RP79; Jackson and McDonald, BS J. Research **6**, 709 (1931) RP299.
[4] Helv. Chim. Acta **9**, 809 (1926).
[5] BS J. Research **11**, 627 (1933) RP611.

rides are hydrolyzed by acid, but their amount can be kept at a minimum by cooling the acidified solution immediately upon the completion of the hydrolysis.

Incomplete hydrolysis, on the other hand, leaves soluble products which not only constitute a loss of potential levulose, but by their solvent effect on calcium levulate cause a further loss of levulose, which, but for their presence, could be avoided. To avoid excessive or deficient conversion a careful control of the hydrolysis reaction is therefore of the first importance.

If after completion of the hydrolysis the defecation is carried out in too highly alkaline solution, or if the temperature is too high, or if as a result of inadequate agitation local high alkalinities occur, levulose may undergo the Lobry de Bruyn-van Ekenstein transformation to dextrose and mannose, resulting in a loss of levulose by decomposition and by the solvent effect of the products of the decomposition on calcium levulate.

The plant juices from which levulose can be obtained usually have a total sugar purity of about 85 percent. Conceivably the nonsugars have a solvent effect upon calcium levulate, but thus far it has proved difficult to separate them from the sugars and no attempt has been made to measure their influence.

Since dextrose is in most instances the predominating impurity its solvent effect on calcium levulate was studied in detail. The experiments were conducted in a metal container holding about 1,800 ml, which was immersed in a large water bath whose temperature was controlled by manual operation. The container was half filled with water, and alternate additions were made of lime and invert sugar in the manner previously described until the container was filled. About one-half of the resulting suspension of levulate was filtered and the filtrate or "waste water" subjected to analysis.[6] The container was again filled by adding reactants to the remaining portion of the levulate suspension and again half was filtered for analysis of the waste water. This process was repeated 4 or 5 times at each of three temperatures. There resulted in each series an accumulation of dextrose.

The experimental results are given in table 1, which shows the composition of the waste waters saturated with calcium levulate. The amount of levulose held in solution as levulate varies with the concentration of dextrose, although not linearly, since the ratio of levulose to dextrose is not constant at all concentrations of sugar. It will be found significant to evaluate these ratios as well as the concentrations of sugar in the succeeding sections of this paper, but they will be expressed as ratios of levulose to total reducing sugar rather than as levulose to dextrose.

At each temperature the ratios of levulose to total reducing sugar are relatively higher in the more dilute solutions of dextrose and approach constant low values as the concentration of dextrose increases. Calcium levulate has an appreciable solubility in water and the solvent effect of dextrose is superimposed upon this. At the higher concentrations of dextrose the latter becomes the predominating effect.

[6] For analytical methods see BS J. Research **8**, 403 (1932) RP426; **9**, 597 (1932) RP495.

TABLE 1.—*Composition of waste water from calcium-levulate precipitate from invert sugar, showing effect of dextrose and of temperature*

Temperature	Reducing sugar	Levulose	Dextrose by difference	Ratio, levulose to reducing sugar	CaO	Ratio, CaO to reducing sugar
°C	g/100 ml	g/100 ml	g/100 ml		g/100 ml	
5	1.587	0.289	1.298	0.182	0.375	0.236
	2.642	.362	2.280	.147	.585	.221
	3.670	.477	3.193	.130	.784	.188
	4.772	.616	4.156	.129	.998	.209
10	1.830	.392	1.438	.214	.393	.215
	3.142	.597	2.545	.190	.605	.192
	4.464	.795	3.669	.178	.850	.190
	5.190	.830	4.360	.160	1.076	.207
	6.262	.996	5.266	.159	1.311	.209
15	1.555	.428	1.127	.275	.347	.223
	3.028	.787	2.241	.260	.565	.187
	4.297	.984	3.313	.229	.821	.191
	5.269	1.175	4.094	.223	1.041	.198
	6.421	1.458	4.963	.227	1.297	.202

Since, as appears from the tabulated values, the lowest ratios in the waste water occur at the highest concentrations of dextrose, the greater yields of precipitated levulate from a given mixture of sugars are obtainable at the higher concentrations of reactants.

The effect of elevated temperature is a considerable increase in the solubility of the levulate, a 10° C rise causing a 75-percent increase in the ratio at its constant low value.

For later reference it will prove of interest to compute by extrapolation that at the lowest concentration of total sugar the ratio at 0° C would be about 0.15, and that under the same conditions a weight of levulose equal roughly to one-fifth of the weight of dextrose remains in solution.

The alkalinity of the waste water is directly proportional to the concentration of total reducing sugar. Independently of temperature 1 g of total sugar holds in solution about 0.2 g of CaO (column 7, table 1). The lime in the waste water is derived not alone from the calcium levulate, but is also dissolved by the water and dextrose.

In table 2 is shown the effect of temperature upon the yield of levulose from artichoke juices in which the ratio of levulose to total reducing sugar was 76.8 percent. The data show that the yield diminishes very rapidly as temperature is increased.

TABLE 2.—*Effect of temperature of reaction upon yield of levulose*

[Hydrolyzed artichoke juices. Ratio, levulose to total reducing sugar, 76.8 percent]

Precipitation temperature	Reaction mixture				Levulate cake			Yield of levulose
	Weight	Reducing sugar	Levulose		Weight	Levulose		
°C	g	%	%	g	g	%	g	%
3.2	1,855	7.33	5.63	104.4	444	19.57	86.9	82.3
10.7	1,800	7.16	5.50	99.0	328	22.98	75.4	76.2
16.0	1,496	7.03	5.40	80.8	249	20.75	51.7	64.0

The solvent effect of the isomeric difructose anhydrides on calcium levulate is illustrated by the analysis of the waste water from the precipitation of levulate at 0° C from pure inulin which had been hydrolyzed by sulphuric acid, the latter being subsequently removed as barium sulphate. The main purpose of the experiment was the estimation and isolation of the difructose anhydrides. The waste water was not analyzed directly but was subjected to a preliminary evaporation. Nevertheless, the pertinent ratios remained unaltered by this treatment.

The waste water from the levulate was exactly neutralized with oxalic acid and the filtered solution evaporated to about 10° Brix. Total solids were determined densimetrically, the total reducing sugars and levulose by the respective copper reduction methods, and the difructose anhydrides by difference. The evaporated solution contained in 100 ml 10.685 g solids, 5.260 g total reducing sugar, of which 3.351 g was levulose, and by difference 5.425 g of difructose anhydrides. The ratio of levulose to total reducing sugar was 0.64, a quantity far too great to be ascribed to the dextrose, as can be seen by reference to table 1. The excessive quantity of levulose is evidently held in solution by the difructose anhydrides. Previous to the discovery of these sugars the high ratio of levulose in the waste water from hydrolyzed inulin was unexplained. If the weight of difructose anhydrides is added to the weight of reducing sugar the computed ratio of levulose to total sugar proves to be 0.314, which indicates that a higher solvent effect is to be ascribed to the anhydro sugars than to dextrose. In crude juices no analytical method for the determination of the difructose anhydrides is available, but a departure of the ratios of levulose to total reducing sugar from those given in table 1 is an indication of their presence or of course the presence of other sugars not detectable by analysis.

In a few experiments on artichoke juices the action of the sulphuric acid was accidentally prolonged after the completion of the hydrolysis of the polysaccharides. The value of the ratio of levulose to reducing sugar in the waste water from the levulate precipitation rose to 0.58 in one instance, showing that the fructosans of Pictet and Chavan had been formed in considerable quantity by the action of the acid.

In table 3 are shown the results of systematic experiments on pure sugars and plant juices in which each of the four products, namely, the reaction mixture, waste water, wash, and levulate cake, was weighed and analyzed. The reaction mixture was prepared in the usual manner, sampled for analysis, and finally weighed. It was then filtered on a Büchner funnel and the waste water collected in a tared filter flask. When the waste water had drained to the surface of the levulate cake the filter flask was replaced by a second one for collection of the wash. In some instances the wash water (that is, the pure water used for washing) was weighed, in others its weight was determined by difference, the latter weights being indicated in the table by brackets.

Each of the four products was analyzed for the three constituents, levulose, total reducing sugar, and lime. The percent concentrations shown by the analyses are given in the left of the subdivided columns in table 3. Although these analytical data were obtained in small-

TABLE 3.—*Quantitative data on calcium levulate precipitation*

Line	Item	1 Pure sugars 0.0		2 Artichokes 1.0		3 Artichokes 1.5		4 Artichokes 3.0		5 Artichokes 0.5		6 Chicory 3.0		7 Dahlias 0.8		8 Artichokes 10		9 Artichokes 9.5	
1	Experiment																		
2	Type of juice																		
3	Temperature of reaction (° C)																		
4	Weight of products, grams:																		
5	Reaction mixture	1,811		1,554		1,715		1,735		1,448		1,644		1,549		1,566		1,838	
6	Waste water	1,199		934		1,121		1,170		849		993		770		1,050		1,234	
7	Wash	724		731		676		705		795		702		675		589		605	
8	Levulate cake	426		444		349		382		406		462		592		394		387	
9	Wash water	(538)		(555)		433		(522)		600		(513)		488		472		400	
10	Product balances:																		
11	Levulose:	%	g	%	g	%	g	%	g	%	g	%	g	%	g	%	g	%	g
12	Reaction mixture	5.38	97.4	8.12	126.1	6.20	106.3	5.88	102.0	5.60	81.2	7.04	115.7	8.92	138.2	6.01	94.2	5.94	109.1
13	Waste water	.23	2.8	1.04	9.7	.91	10.2	.73	8.5	.58	4.9	.84	8.4	.56	4.3	1.25	13.1	1.17	14.4
14	Wash	.23	1.7	.71	5.2	.65	4.4	.47	3.3	.45	3.6	.69	4.8	.49	3.3	.86	5.1	.85	5.1
15	Levulate cake	21.84	93.0	24.10	107.0	26.58	92.8	23.5	89.6	17.71	72.0	21.90	101.2	22.02	130.4	19.29	76.0	22.80	88.2
16	Total recovered	------	97.5	------	121.9	------	107.4	------	101.4	------	80.5	------	114.4	------	138.0	------	94.2	------	107.7
17	Total reducing sugar:																		
18	Reaction mixture	6.55	118.6	10.42	161.9	6.82	117.0	6.80	118.0	6.40	92.8	8.02	131.8	9.55	147.9	8.29	129.9	6.92	127.1
19	Waste water	1.56	18.7	3.70	34.6	2.02	22.7	1.67	19.5	1.52	12.9	1.88	18.7	1.20	9.3	3.55	37.3	2.23	27.5
20	Wash	1.10	7.9	2.19	16.0	1.32	8.9	1.08	7.6	1.00	7.9	1.39	9.8	1.02	6.9	2.34	13.8	1.77	10.7
21	Levulate cake	21.84	93.0	24.10	107.0	26.58	92.8	23.5	89.6	17.71	72.0	21.90	101.2	22.02	130.4	19.29	76.0	22.80	88.2
22	Total recovered	------	119.6	------	157.6	------	124.4	------	116.7	------	92.8	------	129.7	------	146.6	------	127.1	------	126.4
23	Total CaO:																		
24	Reaction mixture	2.53	45.7	3.45	53.6	3.66	62.9	2.71	47.1	3.71	53.7	3.23	53.0	4.00	62.0	3.37	52.7	3.51	64.6
25	Waste water	.37	4.4	1.01	9.4	.69	7.7	.73	8.5	.58	4.9	.67	6.6	.62	4.7	1.01	10.6	.68	8.4
26	Wash	.30	2.2	.62	4.5	.47	3.2	.49	3.5	.40	3.2	.51	3.6	.51	3.5	.71	4.2	.51	3.1
27	Levulate cake	9.08	38.7	8.70	38.6	14.75	51.5	9.00	34.4	11.40	46.3	9.00	41.6	9.06	53.6	10.1	39.8	13.0	50.5
28	Total recovered	------	45.3	------	52.5	------	62.4	------	46.4	------	54.4	------	51.8	------	61.8	------	54.6	------	62.0
29	Ratio, levulose to total reducing sugar:																		
30	Reaction mixture	0.822		0.779		0.910		0.864		0.874		0.878		0.935		0.725		0.858	
31	Waste water	.150		.281		.448		.439		.384		.448		.424		.352		.522	
32	Wash	.209		.325		.494		.439		.450		.493		.487		.369		.48	
33	Yield of levulose, percent	95.5		84.8		87.3		87.8		88.7		87.5		94.3		80.7		80.7	
34	CaO required (theoretical), grams	35.5		47.2		43.4		39.9		30.5		41.7		48.7		38.4		38.9	
35	CaO used, grams	45.7		53.6		62.9		47.1		53.7		53.0		62.0		52.7		64.6	
36	Ratio, CaO to reducing sugar in waste water	0.235		0.272		0.339		0.438		0.383		0.356		0.511		0.285		0.304	

scale experiments they probably represent closely those which may be expected in a levulose plant of any magnitude.

The percentage of each constituent multiplied by the total weight of each product (given in lines 5 to 8) yielded the weights of the respective constituents shown in the right of the subdivided columns. The sums of the weights of each recovered in the waste water, wash, and cake are shown under the captions "Total recovered" (lines 16, 22, and 28) and may be compared with the corresponding weights taken in the reaction mixture (lines 12, 18, and 24). In most instances the balance is satisfactory.

Experiment 1 shows the product analyses of a mixture of pure levulose and pure dextrose taken in a ratio of levulose to total sugar of 82.2 percent (line 30). A yield of 95.5 percent of levulose was obtained in the washed cake (line 33). Dextrose is here the only impurity which can exert a solvent effect upon the precipitated calcium levulate. In the waste water which contained 1.56 percent of total sugar the ratio of levulose to total sugar was 0.150 (line 31), in agreement with the one which was computed by extrapolating the values in table 1 to 0° C. The ratio of CaO to reducing sugar in the waste water (line 36) is in approximate agreement with the values given in table 1.

The juice used in experiment 2 was obtained from the most commonly occurring variety of Jerusalem artichoke in which the ratio of levulose to total reducing sugar was 0.779 (line 30). The waste water showed a ratio of 0.281 (line 31), a value far higher than that obtained from the pure sugars (0.150) in experiment 1. This greater value of the ratio is to be ascribed to the difructose anhydrides derived from the inulin contained in the juice. Observe further the ratios (line 31) in the waste waters in experiments 3 to 7, which reach values nearly 3 times as great as that in experiment 1.

Pure inulin upon hydrolysis by aqueous acids yields a sugar mixture containing about 92 percent of levulose, 3 percent of dextrose, and 5 percent of difructose anhydrides.[7] The ratio of levulose to total reducing sugar is about 97 percent. A high ratio of levulose to reducing sugar in the plant juice is therefore an indication of high inulin content and also an indication of relatively high concentration of difructose anhydrides after hydrolysis.

The high ratios in the juices taken in the reaction mixtures of experiments 3 to 7 (line 30) indicate that the levulose was derived largely from inulin and that a considerable concentration of difructose anhydride must therefore have been present. The ratios of levulose to total reducing sugar in the waste waters are therefore high. The juice in the reaction mixture of experiment 2 contained less inulin, as shown by the low ratio, and therefore less anhydro sugar is formed upon hydrolysis, and the ratio in the waste water, while nearly twice as great as that from the pure sugars of experiment 1, is relatively low compared with the juices of high inulin content.

Fortunately a high inulin content in plant juices is accompanied by a low dextrose content. Consequently, in spite of the high solvent effect of the anhydro sugars upon calcium levulate, they actually cause a smaller loss of levulose than does the dextrose because their concentration can never become greater than 5 percent of the inulin,

[7] Jackson and Goergen, BS J. Research 3, 27 (1929) RP79; Jackson and McDonald, BS J. Research 6, 709 (1931) RP299.

while the dextrose can amount to as much as 25 percent of the total sugar in juices of low inulin content.

The theoretical weight of lime (line 34) was calculated on the assumption that the waste water and wash were saturated and that the levulose in the cake was combined with 1 molecule of CaO. The total theoretical weight is therefore the sum of the weights in the waste water and wash and 31.1 percent of the weight of levulose in the cake. These weights are shown in table 3, together with the weights actually used (lines 34 and 35). It is probable that in many of the experiments the excess of lime used was unnecessarily great.

The ratio of CaO to reducing sugar in the waste water in experiment 1 is 0.235, the solvent effect being produced by dextrose and levulose solely. In the plant juices the ratio assumes greatly increased values, showing again the solvent effect of the difructose anhydrides.

The concentration of levulose (line 12) which can be used in the reaction mixture depends in great measure on the care and skill exercised in building up the precipitate. As has already been shown in table 1, the higher concentrations give higher yields of levulose, but the hazard of producing a finely divided precipitate difficult to filter is increased.

In the experiments recorded in table 3 a wide range of concentrations (line 12) was used and no difficulty in filtration was encountered. In general, while the yields are dependent upon several variables, the higher concentrations of levulose in the reaction mixture appear to cause the more favorable recoveries. In experiment 2 the low ratio of levulose to reducing sugar would ordinarily cause a low recovery, but by taking a concentration of levulose of 8.12 percent in the reaction mixture a favorable yield was obtained. The strikingly high yield of 94.3 percent obtained from dahlia juices in experiment 7 is the combined result of every favorable circumstance, namely, low temperature, high ratio of levulose to total reducing sugar, and very high concentration of levulose in the reaction mixture. The wash water used was, moreover, somewhat less than the weight of the cake, but the last drainings of the wash were essentially colorless. That washing was adequate is shown by the fact that the ratio of levulose to total sugar in the wash (line 32) rose above that of the waste water (line 31), which indicated that pure levulate was being dissolved.

In table 1 it appeared that dextrose held in solution in the waste water roughly one-fifth of its weight of levulose at the lower temperature and lower concentration. The waste water in experiment 7 of table 3 contained 5 g of dextrose (i. e., the difference between total reducing sugar and levulose). The dextrose is thus responsible for the retention of but 1 of the 4.3 g of levulose found in the waste water, the remaining 3.3 g being held back by the difructose anhydrides.

In experiment 1, in which the difructose anhydrides were absent, there are 15.9 g of dextrose in the waste water and there should therefore be about 3 g of levulose. The analytical data show 2.8 g.

A weight of wash water approximately equal to the weight of the levulate cake is sufficient for effective washing. In the present series the washing was continued somewhat after the appearance of a colorless filtrate. By the washing operation a small amount of levulate cake was dissolved. This is shown, in general, by a higher ratio of levulose to total sugar in the wash than in the waste water (lines 31

and 32). In another experiment, not further described here, the final portion of the wash filtrate was analyzed and was found to have a ratio of levulose to total sugar of 95 percent.

Experiments 8 and 9 show again the diminished yields resulting from an increased temperature of precipitation.

In recapitulation, the conditions which favor high yields of levulose are low temperature, high ratio of levulose to total sugar in the crude product, high concentration during precipitation of levulate, and careful control of hydrolysis and defecation.

The question of low temperature of precipitation is complicated by its economic aspect. To facilitate computation we have ascertained by approximate calorimetric measurement that in the reaction between 1 g of levulose and an excess of milk of lime there is an evolution of about 70 calories, between dextrose and lime milk about 31 calories. The specific heat of milk of lime containing 22.4 percent of CaO was found to be 0.78. Unfortunately we have no experimental data on the specific heat of the defecated juice containing 15 percent of levulose, but a juice containing 23.5 percent of levulose and 6.6 percent of dextrose had a specific heat of 0.77, which permits a rough estimate that a juice of similar purity diluted to 15 percent of levulose would have a specific heat of about 0.85. Obviously more refined data are desirable.

The ratio of levulose to total sugar is subject to control only by selection of varieties of artichokes which have a high ratio. There are in existence many varieties of artichokes among which considerable differences occur in respect of the composition of the juices. Some are characterized by a high ratio of levulose to total sugar and are more valuable as sources of levulose. All varieties apparently show their highest ratio in the early autumn immediately after the plant has matured. The ratio thereafter gradually diminishes by transformation of polysaccharides which are composed of levulose to substances which yield dextrose upon hydrolysis. If the dahlia and chicory could be grown as inexpensively as the artichoke they would be greatly superior as sources of levulose.

III. PURITIES OF THE DERIVED LEVULOSE SOLUTIONS

The preparation of the calcium levulate described in the preceding paragraphs was carried out with care, and yet upon suspension in water, carbonation, and evaporation, the levulose sirups emerging from the process showed apparent purities of but 91 to 97 percent, as in the original investigation. It became evident that so great an amount of impurity could not have been retained in the levulate cake, for a simple calculation showed that if the cake had been left unwashed a purity of about 94 percent would have resulted. The thorough washing which the levulate cakes actually received should have removed most of the impurity. Careful analysis enabled us to determine the nature of the impurities in the final liquor and led ultimately to their essential elimination. The principal impurities proved to be dextrose, calcium, magnesium, sulphur as sulphates, and aluminum

Consider first the dextrose and its origin. It is improbable that dextrose was precipitated with calcium levulate since the amount found in the final solution was about the same whether we started with invert sugar of 50-percent dextrose purity or with hydrolyzed

inulin of about 3-percent purity. It was thought possible that dextrose was formed by the Lobry de Bruyn-van Ekenstein rearrangement during carbonation of the levulate cake, since during the early stages of the carbonation the liberated levulose dissolved levulate and produced a high alkalinity. We have shown, however, in a previous article [8] that the rearrangement at low temperatures is extremely slow even at far higher alkalinities than are present during carbonation. A solution normal with respect to hydroxyl ions requires about 6 hours for a 1-percent decomposition of levulose, whereas but 5 to 10 minutes was required for the carbonation. It is, moreover, improbable that the alkalinity became as great as normal.

An experiment was carried out in which a great excess of carbon dioxide was used in order to produce a calcium bicarbonate solution, the levulate cake being added in small portions. At no time was the solution alkaline to phenolphthalein and yet the resulting levulose solution showed but 95-percent purity.

It ultimately proved that the dextrose found in the final liquors was formed by the Lobry de Bruyn-van Ekenstein rearrangement during the evaporation of the carbonated solution. The carbonation of the levulate cake was necessarily carried to a point at which an appreciable amount of calcium bicarbonate was formed. The precipitated calcium carbonate was removed by filtration and the filtrate containing calcium bicarbonate evaporated to release carbon dioxide and precipitate the remaining calcium carbonate. It was at this point that the rearrangement occurred, for when calcium carbonate is produced in this way it imparts a pH of 9.0 to 9.5 to the solution.[9] This alkalinity at 40 to 60° C is sufficient to cause the rearragement.[10]

This particular region according to Mathews and Jackson's data is characterized by the great variation of stability of levulose with relatively small changes of pH and temperature. At 40° C and pH 9, 3.1 hours are required for a 1-percent decomposition of levulose; at 60° C the time is diminished to 10 minutes; at pH 10 and 40° C the time is 30 minutes and at 60° C 1.7 minutes. In view of so great a sensitiveness to small changes in conditions it is now not surprising that in previous preparations great fluctuations in the purities of the levulose sirups occurred.

It is probable that in many instances the degradation of the sugar proceeded in appreciable amount to the formation of acids which accounts for the presence of calcium and magnesium in the final sirups.

The sulphates which contaminated the sirup were derived from the calcium sulphate produced during the defecation of the hydrolyzed juice. It proved to be difficult to induce calcium sulphate to precipitate from these solutions even when its concentration was far above its solubility in pure water and even when seeded with gypsum. In one experiment the defecated juice contained 0.96 percent of calcium sulphate after filtration at 24° C, a saturated solution in pure water containing 0.21 percent. The amount remaining in the defecated juice was practically equivalent to the sulphuric acid used for hydrolysis.

During the precipitation process a small quantity of calcium sulphate precipitated with the levulate, possibly because the great

[8] BS J. Research 11, 632 (1933) RP611.
[9] J.Soc.Chem.Ind. 41, 311 (1923).
[10] Mathews and Jackson, BS J. Research 11, 632 (1933) RP611.

excess of calcium ions increased the ion product beyond the solubility product, or possibly by some form of occlusion. In the most favorable instances 0.08 percent of SO_3, based upon dry substance, was found in the final sirups. In one of the less favorable instances 0.2 percent of SO_3 was found present. In the later experiments a quantity of barium carbonate or barium hydroxide slightly in excess of the calculated requirement was added previous to the carbonation of the levulate cake. This method is capable of removing sulphates effectively, although in only one instance did we add the barium in sufficient quantity.

The most persistent impurities which have not thus far yielded to treatment proved to be magnesium and aluminum, together with small quantities of iron and silica. The magnesium was derived from the lime and remained insoluble as magnesium hydroxide during the precipitation and filtration of calcium levulate. During the carbonation step it was converted to carbonate, which had an appreciable solubility (10.6 mg in 100 ml of water) and thus remained in the final solution. It is conceivable that magnesium carbonate contributes as much as or possibly more than calcium carbonate to the alkalinity of the carbonated solution. We propose to experiment further with magnesia-free lime. The aluminum and iron cycle has not been investigated.

Since dextrose formed by rearrangement of levulose was the predominating impurity in the final sirups, it was imperative to remove calcium bicarbonate by some other means than by volatilization of carbon dioxide in order that an alkaline reaction should be avoided during evaporation. In the procedure finally adopted this was done immediately upon completion of the carbonation, which was carried out in cold solution. In practice the carbonation was continued to a point where the solution was acid to phenolphthalein, an excess of carbon dioxide being necessary to decompose the more resistant particles of levulate and to combine with any free lime which might have been present. A very thin lime milk or calcium levulate suspension was then added to transform calcium bicarbonate to carbonate. At first the attempt was made to control this addition by pH measurements, but this method in so thick a suspension proved impracticable. The most delicate control was obtained by the method of conductometric measurement, since the only conducting substance present in considerable quantity was calcium bicarbonate. The conductivity cell which was of a rugged type permitting free circulation of the solution was inserted directly in the carbonated sludge and the lime milk added slowly until the mixture showed a minimum conductivity. A small portion of the original suspension was held in reserve in order that the end point could be readjusted when it was once passed. The calcium was now in the carbonate stage and had its minimum solubility. Similarly the magnesium was precipitated to the extent of the solubility of magnesium carbonate. Incidentally this method of removing bicarbonate corrects in some measure any errors of defecation, for the solution is alkaline to phenolphthalein, a higher pH than occurs in the usual defecated juice. At this point the solution was still cold and no appreciable decomposition occurred.

The sludge adjusted to minimum conductivity was filtered while still cold. The slightly alkaline filtrate was then treated with dilute

oxalic acid to exactly quantitative precipitation of calcium. Here again the acidification was precisely controlled by the conductivity method, the solution being adjusted to a maximum resistance. The adjustment can be made deliberately and results in a quantitative elimination of calcium. Since only enough oxalic acid is required to neutralize a saturated solution of calcium and magnesium carbonates the amount used is small and by rough calculation its cost is but a few hundredths of a cent per pound of levulose. Probably in a large-scale operation the calcium oxalate could be accumulated and the oxalic acid regenerated.

There is of course objection to the use of oxalic acid and it is our purpose to investigate alternative methods in continuation of the work.

At the point of minimum conductivity the pH was approximately 4.7, and rose to about 5.0 upon evaporation to about 20 Brix. A pH measurement was, however, found unsuitable for the control of the oxalic-acid addition since with the elimination of inorganic salts the solution was but weakly buffered and minute quantities of impurities altered the pH profoundly.

We have shown in a previous article [11] that levulose in water solution has a maximum stability at pH 3.3 At pH 5 it is still sufficiently stable to withstand the conditions to which it is subjected during evaporation and crystallization. It would be a simple matter, if necessary, to reduce the pH to 4, at which it is 2½ times as stable as at 5.

After removal of calcium oxalate by filtration the solutions were evaporated to some density at which it is advantageous to refilter, since usually there occurred a further separation of inorganic salts during evaporation. At the time of refiltration about 2 percent of Darco, based on dry substance, was added, resulting always in a considerable improvement in the apparent purity, which was in some instances increased a whole unit. The carbon proved particularly effective in color removal and the final sirups were practically water white even when evaporated to above 80 Brix.

The sirups were subjected to a careful analysis. By application of the Mathews formula [12] it was determined that the liquors were free from dextrose, the results approximating 100-percent ratio of levulose to total sugar within the limits of analytical precision. Dry substance was determined by means of the immersion refractometer and levulose by direct polarization. Ash was determined by incineration below 600° C without the addition of sulphuric acid. Sulphates were determined in the original sirup.

In table 4 are shown the purities which can be obtained by the modification of the process of recovery of levulose from the levulate precipitate. Although some change of procedure was made in each experiment, all embodied the principle of avoiding alkalinity during evaporation. It is evident that the residual impurity consists mainly of inorganic salts, among which magnesium and aluminum predominate.

In the first 2 experiments a sample of lime practically free from magnesia was used. The high quality of the lime is reflected in the high purity and low ash content of the sirup. In the remaining

[11] BS J. Research 11, 619 (1933) RP611.
[12] BS J. Research 8, 433 (1932).

TABLE 4.—*Purities of levulose solutions derived from the calcium levulate process*

Experiment	Raw juice[a]	Purity of filtrate	Purity after addition of 2% of Darco	Ratio, levulose to total sugar	Ash on dry substance	Analysis of ash				
						CaO	MgO	R_2O_3[b]	SO_3	Undetermined
		%	%	%	%	%	%	%	%	%
1	1		99.10		0.25					
2	1		99.21		.28					
3	2	98.70	99.08		.42					
4	2	97.99	99.02		.51					
5[c]			99.27	100.4	.46	6.0	35.1	15.1	17.5	26.3
6	2	97.50	98.26	100.0	.71					
7	2	98.96	99.22	99.4	.51	0	39.0	28.4	6.8	25.8
8	2	98.53	98.93		.53	0	40.1	14.8	1.5	43.7

[a] Raw juice from artichokes. Number 1 had a ratio of levulose to total sugar of 74.2 percent; number 2, 77.0 percent.
[b] Aluminum and iron oxides and substance insoluble in HCl.
[c] Solutions 3 and 4 combined and treated again with 2 percent of Darco.

experiments lime containing about 2 percent of magnesia was used. In experiment 6 the bicarbonate was destroyed by evaporation of carbon dioxide, the solution being kept acid by constant additions of oxalic acid. This procedure allowed most of the magnesium to remain in the sirup, whereas in the remaining experiments much of the magnesium was precipitated as carbonate.

The data in table 4 show that from crude plant juices, which usually have a levulose purity of about 65 percent, final sirups having a purity in excess of 99 percent can be recovered. Moreover, since the residual impurity consists of relatively insoluble inorganic salts, it may prove in further experimentation that they can at a suitable dilution be partially removed by filtration, in which case the purities of the mother liquors from crystallization will remain high. In any case it is evident that sirups of such high purity will yield a considerable amount of crystalline sugar before the final molasses requires recirculation.

IV. PURITY TABLES

The method of determination of the purity of levulose sirups depends upon the degree of purity of the sample. If the substance is uncontaminated by dextrose a direct polarization yields a correct measure of the levulose concentration. If dextrose is also present and is the only optically active or reducing impurity the ratio of levulose to total sugar can be determined by means of the Mathews formula.[13] If other optically active or reducing impurities than dextrose occur in the sample, levulose must be determined by Nyns's selective reduction method.[14] Dry substance is determined most conveniently by density or refractive-index measurement.

For the determination of purity of the solutions obtained by the method described in the present article a determination of the direct polarization and dry substance is generally sufficient.

Since the labor of calculating purities from these observations is considerable, we have sought to facilitate the computation by the preparation of purity tables which permit the transformation of observations to purities in a single operation. The necessary factors

[13] BS J. Research 8, 433 and 442 (1932) RP426.
[14] BS J. Research 8, 422 (1932) RP426.

are given in tables 5 to 7. In table 8 are given some physical properties of levulose solutions and their temperature coefficients. These data, compiled and recalculated from observations published in a previous article,[15] are serviceable for making small adjustments for temperature and for determining concentrations of levulose.

The sample, if necessary, is diluted with sufficient water to yield a polarization in a 2-dm tube within the scale of the saccharimeter. The density or the refractive index is then determined. For determination of the density all weights must be corrected to a vacuum and the volume measurement made at or corrected to exactly 20 or 25° C. A column of density-temperature coefficients is given in table 8 to facilitate making the usually small corrections to either of the standard temperatures.

The refractive index is determined either with an instrument of the Abbe type or with an immersion refractometer. Table 8 gives factors which are applicable only to the arbitrary scale originally proposed by Pulfrich,[16] according to which 14.5=1.33300, 50.0=1.34650, and 100.0=1.36464. If other arbitrary scales are used the readings must either be corrected to Pulfrich's scale or transformed to refractive indices and the latter applied in table 7. Temperature coefficients are given in table 8 to simplify corrections to the standard temperatures.

The direct polarization is made preferably at exactly 20 or 25° C. If made at other temperatures it must be corrected to one of these temperatures. A column of polarization-temperature coefficients in table 8 includes the change in rotation and the change in volume with change of temperature. If the temperature of the quartz wedges differs from that of the solution a correction should be applied to bring the temperature of the quartz to the temperature of the solution before the coefficients in table 8 are applied. The correction for

TABLE 5.—*Factors for obtaining purities from direct polarization and density*

[Polarization in 2-dm column and density must be observed at or corrected to the same temperature, either 20 or 25° C. Opposite the corrected density find the factor by interpolation. Substitute the factor and the corrected polarization and density in eq 1 or 2]

$$\frac{\text{Factor} \times \text{polarization at } 20^\circ \text{ C}}{100(D_4^{20} - 0.99823)} = \text{percentage purity.} \quad (1)$$

$$\frac{\text{Factor} \times \text{polarization at } 25^\circ \text{ C}}{100(D_4^{25} - 0.99708)} = \text{percentage purity.} \quad (2)$$

$D_{4^\circ}^{20 \text{ or } 25}$	Factor		$D_{4^\circ}^{20 \text{ or } 25^\circ}$	Factor	
	20° C	25° C		20° C	25° C
1.000	7.335	7.516	1.040	7.214	7.396
1.005	7.320	7.501	1.045	7.198	7.380
1.010	7.305	7.487	1.050	7.182	7.363
1.015	7.290	7.472	1.055	7.165	7.345
1.020	7.275	7.458	1.060	7.148	7.327
1.025	7.260	7.444	1.065	7.130	7.309
1.030	7.245	7.429	1.070	7.112	7.290
1.035	7.230	7.412	1.075	7.093	7.271

[15] BS J. Research 8, 403 (1932) RP426.
[16] Z. angew. Chem. p. 1186 (1899).

quartz is 0.000144° S per degree temperature per saccharimeter degree. If the temperature of the wedges is higher than that of the solution the correction is to be added; that is, the negative rotation of the solution is to be increased to a higher negative value. No correction is made for concentration of sugar.

Having determined the polarization and either density or refractive index, substitute the corrected observations in the respective equations in tables 5 to 7 for the determination of purity.

TABLE 6.—*Factors for obtaining purities from direct polarization and refractive index*

[Polarization in 2-dm column and refractive index must be observed at or corrected to the same temperature, either 20 or 25° C. Opposite the corrected refractive index find the factor by interpolation. Substitute the factor and the corrected polarization and refractive index in eq 3 or 4]

$$\frac{\text{Factor} \times \text{polarization at } 20° \text{ C}}{100(n_D^{20} - 1.33300)} = \text{percentage purity.} \quad (3)$$

$$\frac{\text{Factor} \times \text{polarization at } 25° \text{ C}}{100(n_D^{25} - 1.33250)} = \text{percentage purity.} \quad (4)$$

n_D	Factor		n_D	Factor	
	20° C	25° C		20° C	25° C
1.333			1.347	2.629	2.704
1.334	2.664	2.760	1.348	2.626	2.699
1.335	2.661	2.754	1.349	2.622	2.695
1.336	2.659	2.749	1.350	2.619	2.691
1.337	2.656	2.742	1.351	2.615	2.687
1.338	2.654	2.737	1.352	2.611	2.684
1.339	2.651	2.732	1.353	2.608	2.680
1.340	2.649	2.728	1.354	2.604	2.676
1.341	2.646	2.724	1.355	2.600	2.671
1.342	2.642	2.720	1.356	2.596	2.667
1.343	2.640	2.717	1.357	2.592	2.664
1.344	2.636	2.713	1.358	2.589	2.660
1.345	2.634	2.711	1.359	2.585	2.657
1.346	2.632	2.708	1.360	2.581	2.654

TABLE 7.—*Factors for obtaining purities from direct polarization and immersion refractometer readings*

[The factors are applicable only to readings made on refractometers whose arbitrary scale corresponds to Pulfrich's definition; thus, 14.50=1.33300, 50.0=1.34650, 100=1.36464. Polarization in 2-dm column and refractive index must be made at or corrected to the same temperature, either 20 or 25° C. Opposite the corrected immersion reading find by interpolation the factor. Substitute the factor and the corrected polarization and immersion reading in eq 5 or 6]

$$\frac{\text{Factor} \times \text{polarization at } 20° \text{ C}}{\text{Immersion reading at } 20° \text{ C} - 14.50} = \text{percentage purity.} \quad (5)$$

$$\frac{\text{Factor} \times \text{polarization at } 25° \text{ C}}{\text{Immersion reading at } 25° \text{ C} - 13.25} = \text{percentage purity.} \quad (6)$$

Immersion refractometer reading at 20 or 25° C	Factor		Immersion refractometer reading at 20 or 25° C	Factor	
	20° C	25° C		20° C	25° C
15	68.75	70.60	45	69.11	70.99
20	68.83	70.70	50	69.15	71.00
25	68.90	70.79	60	69.20	71.02
30	68.96	70.87	70	69.23	71.03
35	69.02	70.93	80	69.25	71.04
40	69.07	70.97	90	69.25	71.05

TABLE 8.—*Physical properties of levulose solutions*

Concentration (g/100g of solution)		Levulose in 100 ml (vacuum) at—		Levulose in 100 ml (air, brass weights) at—		$\frac{\Delta(g/100\ ml)}{\Delta T}\times 10^{-6}\times(-1)$	D_4^{20} (vacuum)	D_4^{25} (vacuum)	Weight of 1 ml (air, brass weights) at—		$-\frac{\Delta D}{\Delta T}\times 10^{-6}$	n_D^{20}	n_D^{25}	$\frac{\Delta n}{\Delta T}\times 10^{-6}\times(-1)$	Immersion readings at [1]		$\frac{\Delta Imm.}{\Delta T}$	Polarization [2] at—		$-\frac{\Delta Pol.^3}{\Delta T}\times(-1)$
True (in vacuum)	Apparent (in air *vs.* brass weight)	20° C	25° C	20° C	25° C				20° C	25° C					20° C	25° C		20° C	25° C	
%	%	g	g	g	g				g	g								°S	°S	
0	0	0	0	0	0	0	0.99823	0.99708	0.99717	0.99602	231	1.33300	1.33252	96	14.50	13.25	0.250	0	0	0
1	1.0004	1.0021	1.0010	1.0015	1.0003	24	1.00214	1.00095	1.00108	0.99989	238	1.33442	1.33393	98	18.18	16.90	.256	5.33	5.15	0.036
2	2.0009	2.0121	2.0097	2.0109	2.0085	49	1.00607	1.00484	1.00501	1.00378	245	1.33585	1.33535	100	21.87	20.58	.262	10.72	10.35	.073
3	3.0013	3.0301	3.0263	3.0282	3.0245	76	1.01003	1.00877	1.00897	1.00771	252	1.33729	1.33678	102	25.63	24.29	.268	16.15	15.60	.110
4	4.0017	4.0561	4.0509	4.0536	4.0484	104	1.01402	1.01272	1.01296	1.01166	259	1.33874	1.33822	104	29.43	28.06	.274	21.65	20.91	.147
5	5.0021	5.0901	5.0835	5.0870	5.0804	133	1.01803	1.01670	1.01698	1.01565	266	1.34020	1.33967	106	33.27	31.88	.280	27.19	26.27	.184
6	6.0025	6.1324	6.1243	6.1287	6.1205	164	1.02207	1.02071	1.02102	1.01966	273	1.34167	1.34113	108	37.14	35.72	.286	32.80	31.69	.222
7	7.0029	7.1830	7.1733	7.1786	7.1689	196	1.02614	1.02475	1.02509	1.02370	280	1.34315	1.34260	110	41.06	39.62	.292	38.46	37.16	.260
8	8.0033	8.2419	8.2305	8.2369	8.2255	230	1.03024	1.02881	1.02919	1.02776	287	1.34464	1.34408	112	45.04	43.54	.298	44.19	42.69	.299
9	9.0037	9.3093	9.2961	9.3037	9.2905	265	1.03437	1.03290	1.03332	1.03185	294	1.34615	1.34558	115	49.06	47.54	.304	49.97	48.28	.338
10	10.0040	10.3853	10.3702	10.3790	10.3639	301	1.03853	1.03702	1.03748	1.03597	301	1.34766	1.34708	117	53.13	51.56	.312	55.81	53.93	.377
11	11.0044	11.4698	11.4530	11.4628	11.4460	339	1.04271	1.04118	1.04166	1.04013	308	1.34918	1.34858	119	57.21	55.59	.320	61.72	59.64	.417
12	12.0047	12.5630	12.5442	12.5554	12.5366	378	1.04692	1.04535	1.04587	1.04430	315	1.35071	1.35010	121	61.34	59.70	.328	67.70	65.41	.457
13	13.0051	13.6651	13.6441	13.6568	13.6359	420	1.05116	1.04955	1.05011	1.04850	323	1.35225	1.35163	123	65.53	63.83	.336	73.74	71.25	.498
14	14.0054	14.7760	14.7529	14.7670	14.7439	462	1.05543	1.05378	1.05438	1.05273	330	1.35380	1.35317	125	69.77	68.02	.344	79.84	77.15	.539
15	15.0057	15.8958	15.8706	15.8861	15.8610	506	1.05972	1.05804	1.05867	1.05699	337	1.35535	1.35471	127	74.05	72.27	.352	86.02	83.11	.581
16	16.0061	17.0248	16.9973	17.0144	16.9869	552	1.06405	1.06233	1.06300	1.06128	345	1.35692	1.35627	129	78.38	76.58	.360	92.26	89.15	.623
17	17.0064	18.1628	18.1329	18.1518	18.1219	598	1.06840	1.06664	1.06735	1.06559	352	1.35850	1.35784	132	82.78	80.95	.368	98.58	95.25	.667
18	18.0067	19.3100	19.2776	19.2983	19.2659	648	1.07278	1.07098	1.07173	1.06993	360	1.36009	1.35943	135	87.21	85.31	.376	104.97	101.42	.711
19	19.0070	20.4666	20.4316	20.4542	20.4192	697	1.07719	1.07535	1.07614	1.07430	367	1.36170	1.36103	137	91.67	89.74	.385	------	------	------
20	20.0073	21.6324	21.5950	21.6193	21.5819	750	1.08162	1.07975	1.08057	1.07871	375	1.36333	1.36263	139	96.17	94.20	.394	------	------	------

[1] Referable solely to the scale of arbitrary units proposed by Pulfrich, Z. angew. Chem. p. 1,186 (1899). According to this scale, 14.5=1.33300; 50.0=1.34650; and 100.0=1.36464.

[2] Polarization in 2-dm column in saccharimeter whose scale conforms to the specification that the normal quartz plate rotates 40.690° for λ=5,461 A, and 34.620° for λ=5,892.5 A at 20° C.

[3] These coefficients include the change of volume as well as change of rotatory power. They can be applied directly to give the rotation of the solution at either of the standard temperatures.

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HEAT OF COMBUSTION OF ISOBUTANE

By Frederick D. Rossini

ABSTRACT

The data of the present investigation yield for the heat evolved in the combustion of gaseous isobutane in oxygen to form gaseous carbon dioxide and liquid water, at 25° C and a constant pressure of 1 atmosphere, the value 2871.06 ± 0.53 international kilojoules per mole. With the factor 1/4.1833, this value becomes 686.31 ± 0.13 kilocalories per mole. The isobutane used was estimated to be of such purity that its heat of combustion would differ from that of an absolutely pure sample by less than 0.01 percent. The only previous determination of the heat of combustion of isobutane was that made by Thomsen over 50 years ago on some impure material. From these new data values are computed for the heat of formation of isobutane.

When combined with the previously reported data on the heat of combustion of normal butane, the present data yield for the reaction, n-C_4H_{10} (gas) = *iso*-C_4H_{10} (gas), at 25° C and 1 atmosphere, $\Delta H = -6.82 \pm 0.63$ kilojoules, or -1.63 ± 0.15 kilocalories, per mole.

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I. INTRODUCTION

This paper is a report on the calorimetric determination of the heat of combustion of isobutane, which investigation is part of the program of work being carried on by the thermochemical laboratory of the National Bureau of Standards on the accurate measurement of the heats of chemical reactions that are important to industry and science.

An accurate value for the heat of combustion of iosbutane will provide a reliable heating value for this gas when used as a fuel; will permit evaluation of its heat of formation to be used in thermodynamic calculations on the reactions of cracking, dehydrogenation, etc., in which isobutane may take part; when combined with the similar data on normal butane, will yield a reliable value for the energy of isomerism of the two butanes; when combined with appropriate other data, will yield values of the bond energies in the molecule;

and, when combined with values of the entropy, will yield a reliable value for the free energy of formation.

There is extant in the literature only one report on the heat of combustion of isobutane, that published by Thomsen [1] [1] in 1886. The samples of isobutane that Thomsen had available were very impure, one sample having the empirical formula $C_4H_{9.75}$ instead of C_4H_{10}.

Because it is today possible to prepare isobutane of very high purity, and because the accuracy of present-day calorimetric measurements is considerably greater than was possible half a century ago, it was very desirable that a new determination of this thermochemical constant be made.

II. UNITS OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy employed in this work, as in all previous publications from this laboratory, is the international joule, based upon standards of emf and resistance maintained at this Bureau. In order to report the results in calories, as well as in the fundamental unit of electrical energy, values in international joules are converted to a conventional defined calorie by means of the selected factor 1/4.1833. This is the same factor used in the previous conversions [2].

As in the previous work on the hydrocarbons, the thermal data obtained are independent of the atomic weight of carbon, 1 mole of isobutane being taken as equivalent to 5(18.0156) g of water formed in the combustion [2].

III. METHOD, APPARATUS, AND PROCEDURE

The same calorimetric method, apparatus, and procedure were employed in these experiments as were used for the experiments on normal butane.

The sample of isobutane was obtained from the same source, prepared in the same manner, and tested for purity by the methods used on normal butane [2].

The data shown in table 1, obtained by Martin Shepherd, indicate the nature of the possible impurities. The amount of any impurity in mole fraction of the entire sample, is of the order of 1/10 the value of ΔX_2.

Six experiments on the determination of the ratio of carbon to hydrogen in the isobutane gave the following results: Average amount of isobutane used per experiment, 0.025 mole; average value of the ratio 10C/4H, 1.00008; average deviation from the mean, ±0.00008; maximum deviation from the mean, 0.00014. In obtaining the foregoing ratio, the masses of carbon dioxide and water were converted to moles by the use of the values 44.007 and 18.0156, respectively, for the molecular weights [2] [2, 3].

From the manner of preparation of this sample of isobutane, and from the results of the foregoing tests, it appears that the purity of the isobutane was such that, per mole of water formed, its heat of combustion would differ from that of an absolutely pure sample by less than 0.01 percent. (See p. 739–740 of reference [2].)

[1] The numbers in brackets here and elsewhere in the text refer to the references at the end of this paper.

[2] The similar data on normal butane gave 1.00014 ± 0.00012, using 44.000 as the molecular weight of carbon dioxide. Using the value 44.007, the data on normal butane yield 0.99998 ± 0.00012, for the ratio 10C/4H. See page 190 of reference [4].

TABLE 1.—*Data on the purity of isobutane, as shown by measurement of the difference in the vapor pressures between the middle cut and the initial distillate and the final residue, respectively*

Initial distillate[1]			Final residue[1]		
Δp	t	ΔX_2	Δp	t	ΔX_2
mm Hg	°C	*Mole fraction*	mm Hg	°C	*Mole fraction*
13.08	−11.2	0.008 propane	5.20	−10.4	0.016 normal butane

[1] The amounts of the initial distillate and the final residue were respectively, less than 1/20 of the entire sample. The value of ΔX_2 gives approximately the mole fraction of the given impurity in the initial distillate or the final residue, not in the entire sample.

The purity of the combustion reaction in the experiments on isobutane was examined as in the case of normal butane. No carbon monoxide was detected in the products of combustion.

The procedure for determining the amount of reaction in each calorimetric combustion experiment was exactly the same as in the experiments on normal butane, the amount of reaction being determined from the mass of water formed in the combustion. One mole (18.0156 g) of H_2O was taken as equivalent to 1/5 mole of C_4H_{10}.

The experiments made to determine the electrical-energy equivalent of the calorimeter system used for the combustion of isobutane are the same as those for normal butane, and the data are given in table 5 of reference [2]. The correction for "spark" energy was also the same as in the experiments on normal butane.

The calorimetric data of the combustion experiments with isobutane are given in table 2. The "error" of the mean value of the combustion experiments, computed as $\pm 2\sqrt{\Sigma\Delta^2/n(n-1)}$, is ±0.013 percent.

TABLE 2.—*Calorimetric results of the reaction experiments for isobutane*

Experiment	ΔR	k	K	U	$\Delta t_{corr.}$	Avg temp.
	Ohm	min^{-1}	*Ohm*	*Ohm*	°C	°C
1	0.409016	0.001936	0.006180	−0.000122	3.99443	25.00
2	.411889	.001937	.006569	−.000137	4.01920	25.00
3	.410379	.001926	.006319	−.000086	4.00621	25.00
4	.409650	.001920	.006672	−.000106	3.99568	25.00
5	.409141	.001921	.007059	−.000089	3.98663	25.00
6	.410224	.001947	.006832	−.000127	3.99999	25.00
7	.409828	.001945	.006138	−.000084	4.00252	25.00
8	.409531	.001935	.006390	−.000046	3.99670	25.00

Experiment	Electrical energy equivalent of calorimeter system[1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of isobutane	Heat of combustion at 25° C	Deviation from mean
	Int. joules/°C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules/mole*	*Kilojoules/mole*
1	15,237.1	9.5	11.1	218.3	0.0212748	2,871.01	−0.05
2	15,207.4	3.2	12.5	233.2	.0213718	2,870.40	−.66
3	15,223.1	.4	15.1	208.8	.0213081	2,871.26	.20
4	15,217.2	−1.5	17.7	219.0	.0212455	2,871.33	.27
5	15,251.6	2.0	32.8	222.7	.0212507	2,870.23	−.83
6	15,228.1	6.1	19.0	207.6	.0212820	2,871.29	.23
7	15,238.7	2.4	17.0	204.6	.0213050	2,871.78	.72
8	15,205.3	−3.1	13.8	219.0	.0212360	2,871.21	.15
Mean						2,871.06	±.39

[1] Includes the heat capacity of one-half the mass of liquid water formed in the reaction.

IV. RESULTS OF THE PRESENT INVESTIGATION

The uncertainty in the final value obtained from the present data has been computed by taking the total percentage "error" as equal to $\pm\sqrt{e_1^2+e_2^2+e_3^2}$, where e_1 is the percentage "error" of the mean value of the calorimetric experiments with electrical energy, e_2 that of the calorimetric combustion experiments, and e_3 is an "error" of 0.01 percent assumed in the determination of the amount of reaction, due to impurities and other causes.

The data of the present investigation yield for the heat evolved in the combustion of gaseous isobutane in oxygen to form gaseous carbon dioxide and liquid water, at 25° C and a constant pressure of 1 atmosphere, the value 2871.06 ± 0.53 international kilojoules per mole.

V. DATA OF PREVIOUS INVESTIGATIONS

The only previously reported determination of the heat of combustion of isobutane is that of Thomsen [1], made over 50 years ago. Thomsen performed three experiments on isobutane in his flame calorimeter at constant pressure and at an average temperature of about 18.5° C. The first two experiments were made with a sample of isobutane having the empirical formula $C_4H_{9.748}$, and the third with a sample having the formula $C_4H_{9.899}$. Thomsen assumed that the impurity was butene, C_4H_8, and made a correction to his observed data to obtain a value for "pure" isobutane. He reported a value which, when converted to 25° C and the modern unit of energy, yields 685.6 kilocalories per mole. However, the writer has recomputed Thomsen's original calorimetric data, assigning a reasonable uncertainty and making correction for the impurity, unit of energy, etc., and obtains therefrom the value 686.2 ± 1.6 kilocalories per mole for the heat of combustion of isobutane at 25° C and a constant pressure of 1 atmosphere. While this indicates extraordinarily good agreement with the value from the present investigation, the accord must be somewhat fortuitous, since Thomsen's data on methane, ethane, and propane yield values not in accord, within the reasonable limits of error assigned to his work, with the values recently reported from this laboratory.

VI. CONCLUSION

The present data yield for the reaction,

$$iso\text{-}C_4H_{10}\ (\text{gas}) + \frac{13}{2}\ O_2\ (\text{gas}) = 4\ CO_2\ (\text{gas}) + 5\ H_2O\ (\text{liquid}),$$

at 25° C and a constant pressure of 1 atmosphere, $\Delta H = -2{,}871.06 \pm 0.53$ international kilojoules per mole, or, using the factor 1/4.1833, $\Delta H = -686.31 \pm 0.13$ kilocalories per mole.

Utilizing the values for the heats of formation of carbon dioxide and of water given in an earlier paper [3], the following values are obtained for the heat of formation of isobutane at 25° C:

4 C (c, β graphite)+5 H_2 (gas)=*iso*-C_4H_{10} (gas),

$\Delta H^\circ_{298.1}=-32.20\pm0.43$ kilocalories per mole;

4 C (c, diamond)+5 H_2 (gas)=*iso*-C_4H_{10} (gas),

$\Delta H^\circ_{298.1}=-33.08\pm0.43$ kilocalories per mole.

Combination of the present value for the heat of combustion of isobutane with that previously reported for normal butane will yield a reliable value for the difference in the energies of formation of the two isomers. With no significant impurity in the reaction (see page 358), the reliability of the relatively small difference in the two values of the heats of combustion will be determined by the precision of the two values rather than by the absolute accuracy. The precision uncertainties of the calorimetric combustion experiments are, respectively, ±0.018 and ±0.013 percent, or ±0.52 and ±0.37 kilojoule per mole, for normal butane and isobutane. Taking the uncertainty in the difference in the two heats of combustion as the square root of the sum of the squares of the foregoing quantities, one obtains for the following reaction, at 25° C and 1 atmosphere,

n-C_4H_{10} (gas)=*iso*-C_4H_{10} (gas),

$\Delta H_{298.1}=-6.82\pm0.64$ kilojoules, or -1.63 ± 0.15 kilocalories, per mole. Since for the two isomers, at room temperature and a pressure of 1 atmosphere, the values of PV, and of E $(P=1)-E$ $(P=0)$, are not significantly different, one can write for the above reaction $\Delta H^\circ_{298.1}=\Delta E^\circ_{298.1}=-1.63\pm0.15$ kilocalories per mole. This value indicates that at 25° C the internal or intrinsic energy of isobutane is less than that of normal butane by 1.63 ± 0.15 kilocalories per mole. There is extant in the literature no value with which this can be compared.[3]

This new value for the heat of combustion of isobutane has also been utilized in conjunction with the previously reported data [2, 3] on methane, ethane, and propane, to deduce a fairly reliable value for the heat of combustion and of formation of tetramethylmethane (neopentane) [8].

VII. REFERENCES

[1] Thomsen, Thermochemische Untersuchungen, **IV,** (Barth, Leipzig, 1886).
[2] Rossini, BS J. Research **12,** 735 (1934) RP686.
[3] Rossini, J. Research NBS **13,** 21 (1934) RP692.
[4] Rossini, J. Research NBS **13,** 189 (1934) RP701.
[5] Roth and Macheleidt, unpublished. The numerical results appear in the Landolt-Börnstein-Roth-Scheel Tabellen, 5th ed., **II,** 1588. (Springer, Berlin, 1923.)
[6] Landolt-Börnstein-Roth-Scheel Tabellen, 5th ed., second supplement, p. 1634. (Springer, Berlin, 1931.)
[7] Private communication.
[8] Rossini, J. Chem. Phys. **3,** 438 (1935).

WASHINGTON, July 1, 1935.

[3] The values reported by Roth and Macheleidt [5] for the heats of combustion of gaseous normal pentane and isopentane (the difference of which would be expected to give a value in fair agreement with the above) have been withdrawn [6, 7].

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP834

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COMPARATIVE WEAR OF CHROME-TANNED, VEGETABLE-TANNED, AND RETANNED SOLE LEATHER

By Roy C. Bowker and Warren E. Emley

ABSTRACT

The results of actual service tests of commercial leathers show that chrome-tanned sole leather wears longer than vegetable-tanned leather, and that the durabilities of retanned or of combination-tanned leathers lie between the two.

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I. INTRODUCTION

Tanning with salts of chromium has been applied to heavy hides for the production of sole leather in the belief that a product could be obtained which would possess greater resistance to wear than vegetable-tanned leather. Previous work done by this Bureau [1] showed that this belief was justified and that natural chrome-tanned sole leather wore about twice as long as vegetable-tanned sole leather. The chief disadvantage was found to be its loose structure, which accounted for its lack of firmness and its relatively low water resistance.

The presentation of these results was followed by a marked activity on the part of tanners in the preparation of sole leathers tanned, in part, with salts of chromium. Numerous leathers appeared which were produced by various combinations of the chrome- and vegetable-tanning processes, together with the use of different fillers. All of these leathers were prepared with the object of approaching the firmness and water resistance characteristic of vegetable-tanned leather and utilizing, so far as possible, the increased durability shown to be inherent in chrome leather.

The logical result of this situation was a demand for information by which the success of the new processes could be measured. Consequently, at the solicitation of many interested tanners and in view of the expressed interest of various departments of the Government,

[1] R. C. Bowker and M. N. V. Gelb, *Comparative durability of chrome- and vegetable-tanned sole leathers*, Tech. Pap. BS **19**, 267 (1924-25)T.

TABLE 1.—*Chemical analyses of leathers*

FC = Filled chrome.
NC = Natural chrome.
HRC = Heavy retanned chrome.
LRC = Light retanned chrome.
MRC = Medium retanned chrome.
C = Combination tanned.
FV = Flexible vegetable.
V = Vegetable.

Series	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Leather	FC	NC	FC	NC	NC	NC	HRC	LRC	MRC	C	NC	FC	LRC	C	FC	LRC	HRC	HRC	HRC	FV	FV	FV
Constituent:																						
Water-solubles	15.18	5.85	12.98	No test.	4.64	1.68	23.12	8.36	3.95	21.83	5.37	16.40	21.22	8.90	8.15	7.47	23.00	4.88	23.20	20.30	25.20	28.80
Hide substance	34.75	74.20	34.61	do	86.55	88.15	41.68	63.90	35.40	40.70	75.80	33.25	40.50	43.30	34.80	47.10	37.50	40.60	39.60	41.10	33.70	33.70
Grease (petroleum-ether extract)	22.83	2.73	22.71	do	1.79	1.00	5.34	11.26	37.21	5.46	2.14	21.22	7.99	13.70	24.30	30.20	8.52	15.84	8.28	5.35	15.35	9.00
Insoluble ash	19.47	7.90	------	do	------	6.73	1.52	3.30	2.00	2.94	4.47	17.40	20.80	3.74	20.90	2.68	2.18	3.29	1.97	.20	.28	.23
Combined tannin [1]	------	------	------	do	------	------	28.34	------	21.43	29.07	------	------	9.49	30.36	------	12.55	28.80	35.39	26.95	33.05	25.47	28.27
Total	------	------	------	------	------	------	100.00	------	100.00	100.00	------	------	100.00	100.00	------	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Degree of tannage [2]	------	------	------	No test	------	------	68.10	------	60.70	71.50	16.20	------	23.40	70.20	------	26.60	76.80	87.20	68.00	80.50	75.70	84.00
Glucose	6.03	------	5.54	do	------	------	2.40	------	------	5.98	------	5.12	7.85	------	------	------	.90	------	.90	------	2.77	------
Epsom salts	------	------	------	do	------	------	6.02	------	------	7.96	1.10	7.03	8.10	------	.48	------	1.00	------	3.30	1.08	.66	1.09
Total ash	20.18	9.87	23.19	do	8.00	6.75	4.72	------	2.69	8.29	6.45	25.95	27.10	5.54	------	6.72	5.45	4.16	3.69	2.26	1.18	4.04
Chrome (Cr_2O_3)	5.08	7.22	4.06	do	5.24	5.55	1.47	2.52	1.89	2.43	4.04	3.38	4.18	2.34	2.23	2.48	1.17	2.76	1.27	------	------	------
Barium ($BaSO_4$)	------	------	------	do	------	------	------	------	------	------	------	14.00	15.50	------	------	------	------	------	------	------	------	------

Series	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Leather	V	V	V	V	FC	FC	V	V	V	V	V	LRC	MRC	V	V	V	V	V	V	V	V	V
Constituent:																						
Water-solubles	25.91	29.85	28.45	31.88	No test.	1.60	31.63	No test.	37.50	33.85	28.70	21.22	22.10									
Hide substance	41.25	38.36	39.51	37.67	do	64.35	39.40	do	32.10	33.90	37.80	40.50	39.95									
Grease (petroleum-ether extract)	2.27	2.41	3.24	3.46	do	24.07	3.51	do	5.34	4.57	4.27	7.99	8.99									
Insoluble ash	.15	.20	.50	.42	do	6.04	.15	do	.23	.16	.28	20.80	15.08									
Combined tannin [1]	30.43	29.18	28.30	26.57	do	------	25.31	do	24.82	27.52	28.95	9.49	13.87									
Total	100.00	100.00	100.00	100.00	------	------	100.00	------	100.00	100.00	100.00	100.00	100.00									
Degree of tannage [2]	74.00	76.00	72.00	71.00	No test.	------	64.30	No test.	77.40	81.10	76.60	23.40	34.60									
Glucose	3.64	7.18	3.80	4.66	do	------	7.09	do	9.14	3.94	6.71	7.85	6.83									
Epsom salts	.50	2.17	3.42	------	do	------	5.58	do	6.07	5.94	2.59	8.10	7.24									
Total ash	.42	.90	2.76	2.80	do	6.08	1.99	do	4.58	3.94	2.14	27.10	22.75									
Chrome (Cr_2O_3)	------	------	------	------	do	6.23	------	do	------	------	------	4.18	2.76									
Barium ($BaSO_4$)	------	------	------	------	do	------	------	do	------	------	------	15.50	11.45									

Leather similar to 9V and 10V.

[1] Determined by difference.
[2] Ratio of combined tannin to hide substance.

a study was made to determine the comparative wear of these special leathers and vegetable-tanned leathers.

II. MATERIALS

All of the leathers used in this work were furnished by the tanners and were stated to be strictly commercial materials. Nine lots were vegetable tanned; 3 flexible vegetable; 3 natural chrome; 6 filled chrome; 5 light retanned chrome; 2 medium retanned chrome; 4 heavy retanned chrome; and 2 combination tanned; making a total of 34 lots of leather from 22 tanners. The chemical compositions of these leathers are shown in table 1.

III. TEST METHODS

There is no accepted laboratory method for measuring the durability of sole leather, nor is there any basic standard to which the durability of a given sample can be referred. Recourse was therefore had to the service test, whereby it is possible to get an indication of the comparative durabilities of any two leathers.

The procedure can best be described by following through one series—series 1, for example. This series consisted of 2 lots of leather, 1 vegetable tanned and 1 filled chrome, which were furnished by the same tanner. An equal number of right and left soles were cut from each lot. These soles were paired in such a way that the 2 soles in each pair came from the same location in the hides, and that half of the left soles were vegetable tanned and half of them chrome tanned. The soles were attached to shoes in the Bureau shop (a few were attached in a commercial shop), and were worn by members of the Bureau staff.

Each wearer was required to record the number of hours the shoes were worn, and to bring them in for examination at stated intervals. When one of the soles was found to be worn through, the pair was withdrawn from service. The durability of the worn sole was obtained from the time record kept by the wearer; that of the other sole was estimated from the measured loss of thickness.

In series 1 there were 28 pairs of soles. It was found that on the average the chrome sole would last 80.8 days, the vegetable sole 66.4 days. Since there was some difference in thickness between the original soles, this factor was eliminated by dividing the days worn by the original thickness, to get "days wear per iron".[2] This was found to be 10.1 for the chrome and 8.2 for the vegetable. On the basis of this test, therefore, it can be said with some degree of assurance that the particular filled-chrome leather examined was 23 percent more durable than the particular vegetable-tanned leather with which it was compared.

There were 22 such series in the present work, consisting of a total of 996 pairs of soles. The detailed test results are shown in table 2.

[1] One iron equals 1/48 inch.

TABLE 2.—*Results of wear tests*

Series	Description of leathers compared	Number of pairs of soles tested	Average thickness of soles (irons)[a]	Average days wear per sole	Percentage longer average wear per sole	Average days wear per iron[a]	Percentage longer average wear per iron[a]
1	Filled chrome	28	8.0	80.8	22	10.1	23
	Vegetable		8.1	66.4		8.2	
2[b]	Natural chrome	33	8.0	192.1	72	23.9	111
	Vegetable		9.9	111.5		11.3	
3[b]	Filled chrome	140	8.2	131.2	42	16.0	40
	Vegetable		8.1	92.2		11.4	
4	Natural chrome	63	9.4	195.0	113	20.9	115
	Vegetable		8.7	84.3		9.7	
5	Natural chrome	59	7.2	210.0	20	28.5	21
	Filled chrome		7.4	175.4		23.7	
6	Natural chrome	88	10.5	350.2	5	33.2	11
	Filled chrome		11.1	333.9		30.0	
7[b]	Heavy retanned chrome	89	6.5	71.8	9	11.0	27
	Vegetable		7.6	66.3		8.7	
8	Light retanned chrome	19	8.0	156.0	39	19.4	76
	Vegetable		10.2	112.0		11.0	
9[b]	Medium retanned chrome	131	10.3	160.0	48	15.5	48
	Vegetable		10.3	108.0		10.5	
10[b]	Combination	99	9.4	121.0	22	13.0	31
	Vegetable		10.0	99.0		9.9	
11	Natural chrome	21	8.9	217.5	82	24.4	107
	Vegetable		10.1	119.2		11.8	
12[b]	Filled chrome	39	10.2	145.3	17	14.2	13
	Light retanned chrome		9.8	123.2		12.6	
13[b]	Light retanned chrome	43	8.8	135.5	9	15.3	12
	Medium retanned chrome		9.2	124.7		13.6	
14	Combination	19	12.3	262.0	35	21.3	18
	Vegetable		10.4	193.0		18.1	
15	Filled chrome	14	10.2	246.0	24	23.3	33
	Vegetable		10.9	198.0		17.5	
16	Light retanned chrome	18	11.3	251.0	70	23.0	67
	Vegetable		10.5	148.0		13.8	
17	Heavy retanned chrome	11	8.9	166.0	4	18.7	24
	Vegetable		10.8	160.0		14.2	
18	Heavy retanned chrome	14	10.7	157.0	1	14.7	4
	Vegetable		11.1	158.0		14.2	
19	Heavy retanned chrome	12	8.1	109.9	7	13.4	2
	Vegetable		8.8	117.0		13.1	
20	Flexible vegetable	17	7.5	74.0	16	9.9	5
	Vegetable		8.3	86.0		10.4	
21	Flexible vegetable	20	10.1	144.0	1	14.2	3
	Vegetable		10.6	146.0		13.8	
22	Flexible vegetable	19	10.2	193.0	4	18.9	6
	Vegetable		10.4	185.0		8	

[a] One iron equals 1/48 inch.
[b] From same hide.

IV. DISCUSSION AND SUMMARY

A comparison of the chemical compositions of the leathers with their relative durabilities indicates certain tendencies. In general, the greater the percentage of hide substance the greater the durability; the presence of chrome increases the durability; grease and insoluble ash have little effect; excessive amounts of water-soluble

materials seem to be deleterious. But these are all indications only—the relations are not sufficiently definite to permit expressing them as mathematical formulas.

For definite conclusions, recourse must be had to the names given to the leathers by the manufacturers. The appropriateness of the names can be checked to a certain extent by chemical analysis, and by visual observation, but it is evidently impossible to state definitely that a certain leather is "medium retanned chrome" and not "heavily retanned chrome."

Considering the durability of the vegetable leather as unity, the weighted averages taken from table 2 give the relative durabilities shown in table 3. It must be noted that all of the vegetable leathers used for comparison contained large amounts (over 20 percent) of water-soluble material.

TABLE 3.—*Relative durabilities of different types of sole leather*

[Durability of vegetable tanned leather = 1]

Types of leather	Series	Pairs of soles tested	Relative durability
Flexible vegetable	20, 21, 22	56	1.02
Heavy retanned chrome	7, 17, 18, 19	126	1.22
Combination	10, 14	118	1.29
Filled chrome	1, 3, 15	182	1.37
Medium retanned chrome	9	131	1.48
Light retanned chrome	8, 12, 13, 16	119	1.75
Chrome	2, 4, 5, 6, 11	264	1.77

The data in table 3 show that when the chrome- and vegetable-tanning processes are used either in combination or in succession, the durability of the resultant sole leather will be greater in proportion to the predominance of the chrome tannage.

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INFLUENCE OF SOME SULPHUR-CONTAINING TANNING MATERIALS ON THE DETERIORATION OF VEGETABLE-TANNED LEATHERS BY SULPHURIC ACID

By Everett L. Wallace, Joseph R. Kanagy, and Charles L. Critchfield

ABSTRACT

The influence of a synthetic tanning material, sulphite cellulose, and sulphited extracts on the deterioration of leather, when used with chestnut and quebracho extracts for tanning, was studied. Leathers tanned with the aid of these materials were treated with varying amounts of sulphuric acid and aged under controlled conditions of temperature and relative humidity. Deterioration was determined by measuring the change in tensile strength after 6, 12, 18, and 24 months. The amount of extractable nitrogen was also determined for the samples aged for 24 months. The results show that deterioration as measured by tensile strength and chemical decomposition of the hide substance is a function of the pH value of a water extract of the sample rather than the acid content of the leather as measured by the total sulphur or the Procter and Searle method.

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I. INTRODUCTION

The development and increased use of materials containing sulphur in the production of vegetable-tanned leather has logically led to an investigation of the effects of these materials on the deterioration of the leather, as a function of the acidity, during storage.

Any of the direct analytical methods in use for evaluating the acidity are of doubtful value when applied to leather tanned with materials containing organic sulphur compounds.

In previous work [1] at the National Bureau of Standards on the effect of acid on different leathers during storage, the deterioration has been expressed both as functions of the added sulphuric acid and of the pH value of an aqueous extract of the leather. It was also shown [2] that the amount of added sulphuric acid which would cause serious deterioration in 2 years varied from 0.3 to 1.8 percent for the different leathers, and that the pH of the leather extract had a more definite relation to the loss in strength than did the acid content.

The sulphur-containing substances selected for study in this report were synthetic tanning materials, sulphited quebracho extract, and

[1] BS J. Research **10**, 559 (1933) RP548; J. Am. Leather Chem. Assn. **28**, 125 (1933).
[2] J. Research NBS **14**, 121 (1935) RP761; J. Am. Leather Chem. Assn. **30**, 91 (1935).

sulphite cellulose extract. These products are commonly used in the manufacture of both heavy and light leathers.

II. MATERIALS AND METHODS

The leather used in this work was prepared in the experimental tannery at the National Bureau of Standards from green-salted steer hides and consisted of the following lots; lot 21 (chestnut extract and syntan); lot 22 (quebracho extract and syntan); lot 27 (sulphited quebracho extract); lot 28 (chestnut extract and syntan); lot 29 quebracho extract and syntan); lot 30 (chestnut extract and sulphite cellulose); and lot 31 (quebracho extract and sulphite cellulose). Lots 21 and 22 were tanned with a blend consisting of 25 lb of syntan of 21° Be to 75 lb of the liquid vegetable extracts containing 25 percent of tannin. This is a larger proportion of syntan than is normally used in the production of heavy leather, but was used to assure a high Procter and Searle value. Lot 27 was tanned with sulphited quebracho extract and the pH of the liquors was maintained at approximately 4 by the use of acetic acid. Lots 28 and 29 were tanned with a blend similar to that used for lots 21 and 22, except that the proportion was 10 lb of syntan to 90 lb of liquid vegetable extract. Lot 30 was tanned with a blend consisting of 75 percent of chestnut extract and 25 percent of sulphite-cellulose extract. Lot 31 was similar to lot 30, except that quebracho was used instead of the chestnut extract. The chemical analyses of these leathers before aging are given in table 1.

TABLE 1.—*Chemical Analyses of Leather*

[Results expressed in percentage, excepting for degree of tannage and pH value]

Items determined	Leather lot number and tanning material						
	21—Chestnut syntan	22—Quebracho syntan	27—Quebracho sulphited	28—Chestnut syntan	29—Quebracho syntan	30—Chestnut sulphite cellulose	31—Quebracho sulphite cellulose
Water-soluble	9.19	8.93	8.28	8.40	11.53	10.26	11.04
Hide substance	49.68	47.93	48.95	48.16	45.69	47.22	45.06
Grease (petroleum-ether extract)	3.23	3.89	4.37	3.69	4.73	4.26	2.92
Moisture	11.96	9.97	9.40	11.26	9.91	10.86	9.89
Insoluble ash	.20	.21	.10	.11	.09	.12	.10
Combined tannin [1]	25.74	29.07	28.90	28.38	28.06	27.28	31.08
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Degree of tannage [2]	52.00	61.00	59.00	59.00	61.00	58.00	69.00
Soluble tans	7.87	7.73	6.71	7.10	9.91	8.76	9.55
Soluble nontans	1.32	1.20	1.57	1.30	1.62	1.50	1.48
Total ash	.34	.42	.18	.31	.16	.31	.27
Acid (Procter and Searle)	1.70	1.61	.80	.35	.41	.62	.70
pH value [3]	3.62	4.36	3.90	4.07	4.58	3.72	4.04

[1] Determined by difference.
[2] Ratio of combined tannin to hide substance.
[3] 5 g of leather in 100 ml of distilled water.

The different lots of leather were divided into 4 groups for acid treatment and aging. The original tensile strength of the leather was determined by the average of 2 specimens cut from each block. The leather was then treated with acid, air dried, and after conditioning at 65-percent relative humidity, and tensile strengths of

2 more specimens from each block were measured to determine the immediate effect of the treatment. The blocks containing no added acid, used for determining the normal aging of the leather, were treated with water. The method of sampling was similar to that described by Bowker, Wallace, and Kanagy in their report on the influence of magnesium sulphate on the deterioration of vegetable-tanned leather by sulphuric acid.[3]

The original pH values and sulphuric-acid content of the different lots of leathers are given in table 2.

TABLE 2.—*Original* pH *Values and Sulphuric-Acid Content of the Leathers*

Leather lot number and tanning material	Sample number	Original pH	Percentage of sulphuric acid in dry leather					
			Method					
			Procter and Searle		Oxygen bomb		Nitric acid bromine	
			Total	Added	Total [1]	Added [2]	Total [1]	Added [2]
21—Chestnut syntan	0	3.62	1.70	0.00	----------	----------	0.72	0.00
	1	2.64	2.30	0.60	----------	----------	1.68	0.96
	2	2.18	3.20	1.50	----------	----------	2.48	1.76
	3	1.94	4.20	2.50	----------	----------	3.50	2.78
22—Quebracho syntan	0	4.36	1.61	0.00	----------	----------	0.65	0.00
	1	2.94	2.21	0.60	----------	----------	1.49	0.84
	2	2.28	3.28	1.67	----------	----------	2.57	1.92
	3	1.98	4.11	2.50	----------	----------	3.44	2.79
27—Sulphited quebracho	0	3.90	0.80	0.00	2.30	0.00	1.65	0.00
	1	2.76	1.59	0.79	3.10	0.80	2.54	0.89
	2	2.35	2.34	1.54	3.86	1.56	3.18	1.53
	3	2.15	3.06	2.26	4.62	2.32	3.94	2.29
28—Chestnut syntan	0	4.07	0.35	0.00	1.02	0.00	0.10	0.00
	1	3.01	1.08	0.73	1.82	0.80	0.88	0.78
	2	2.65	1.74	1.39	2.60	1.58	1.62	1.52
	3	2.38	2.40	2.05	3.50	2.48	2.48	2.38
29—Quebracho syntan	0	4.58	0.41	0.00	0.89	0.00	0.28	0.00
	1	3.13	0.96	0.55	1.66	0.77	1.03	0.75
	2	2.64	1.77	1.36	2.45	1.56	1.83	1.57
	3	2.40	2.25	1.84	3.07	2.18	2.47	2.19
30—Chestnut sulphite cellulose	0	3.72	0.62	0.00	2.44	0.00	1.74	0.00
	1	2.67	1.20	0.58	3.16	0.72	2.35	0.61
	2	2.33	1.88	1.26	3.94	1.50	3.12	1.38
	3	2.03	2.80	2.18	4.59	2.15	3.68	1.94
31—Quebracho sulphite cellulose	0	4.04	0.70	0.00	2.48	0.00	1.57	0.00
	1	2.89	1.23	0.53	3.19	0.71	2.35	0.78
	2	2.33	2.27	1.57	3.90	1.42	3.13	1.56
	3	2.04	2.80	2.10	4.68	2.20	3.87	2.30

[1] Sulphuric acid calculated from the total sulphur in the sample.
[2] Sulphuric acid added, calculated from the difference in acid content of the sample before and after treatment.

The amount of acid added was determined by the difference between the calculated amount of acid in the original sample and in the sample after treatment. The acid was determined by the following methods: Modified Procter and Searle; complete combustion of the sample in an oxygen bomb and a subsequent gravimetric determination of the sulphates in the bomb washings; and by oxidation of the sample with nitric acid and a gravimetric determination of the sulphates formed.

[3] J. Research NBS **14**, 121 (1935) RP761; J. Am. Leather Chem. Assn. **30**, 91 (1935).

It is shown in table 2 that the agreement between the bomb and the nitric-acid methods is close for the calculated amount of acid added to the samples, but that the acid calculated from the total sulphur in the sample before treatment is much higher by the bomb method. This indicates that certain sulphur compounds in these leathers are resistant to oxidation by the nitric-acid treatment.

III. RESULTS AND DISCUSSION

The results for the tensile strength determinations for the different leathers and aging periods are given in table 3.

TABLE 3.—*Results of tensile strength determinations of leathers aged at 70° F, calculated in pounds per square inch*

Lot 21 Aged at 65-Percent Relative Humidity

Sample number	Untreated	Age of treated samples in months				
		0	6	12	18	24
0	3872	* 3739	3615	3550	3556	3322
1	4218	3572	3378	3546	3172	3270
2	4058	3273	2964	2848	2616	2295
3	4270	3111	2101	1516	1221	1271
Lot 21 Aged at 85-Percent Relative Humidity						
0	3670	* 3769	3322	3422	3232	3210
1	4188	3504	3045	2838	2531	2390
2	4158	3280	2658	1826	1528	1363
3	3980	3057	1162	631	515	488
Lot 22 Aged at 65-Percent Relative Humidity						
0	4718	* 4560	4698	4588	4233	4652
1	4850	4748	4491	4476	4438	4688
2	4791	4202	4078	4366	3990	4217
3	5146	4293	3841	3162	2796	3560
Lot 22 Aged at 85-Percent Relative Humidity						
0	4848	* 4837	4445	4692	4323	4520
1	4659	4612	4192	4006	3835	4170
2	5014	4762	4264	3695	3642	3387
3	4738	4095	3065	1877	1500	1437
Lot 27 Aged at 65-Percent Relative Humidity						
0	3467	* 3637	3325	3469	3310	3700
1	3130	3381	3209	3280	3060	3410
2	3430	3424	3138	3162	2915	3211
3	3512	3162	2513	2370	2169	2078
Lot 28 Aged at 65-Percent Relative Humidity						
0	3446	* 3458	3359	3498	3002	3410
1	3415	3246	2851	2973	2762	2826
2	3270	3029	2640	2330	2010	2072
3	3315	2982	2240	1862	1465	1500
Lot 29 Aged at 65-Percent Relative Humidity						
0	3795	* 4090	3970	4102	3661	3940
1	3797	3850	3622	3890	3670	3768
2	3961	3706	3610	3532	3437	3430
3	3822	3545	3285	3290	3113	3002

TABLE 3.—*Results of tensile strength determinations of leathers aged at 70° F, calculated in pounds per square inch*—Continued

Sample number	Untreated	Age of treated samples in months				
		0	6	12	18	24
Lot 30 Aged at 65-Percent Relative Humidity						
0	3079	[a] 3279	3161	3520	2975	3312
1	3121	3094	2902	2972	2706	2836
2	3138	2769	2394	2280	2021	1925
3	3148	2811	1717	1196	872	700
Lot 31 Aged at 65-Percent Relative Humidity						
0	3071	[a] 3250	3360	3389	3338	3360
1	3010	3082	2920	3198	3290	3225
2	3450	3170	3166	3112	3020	3350
3	3313	3138	2689	2360	2240	2190

[a] Treated with water for control.

Lots 21 and 22 were aged at 70° F and at 65- and 85-percent relative humidities. The remaining lots were aged at 70° F and 65-percent relative humidity.

The normal aging for the leathers containing no added acid is shown for the different leathers and aging periods in table 3. The average loss in tensile strength for lot 21, chestnut-syntan leather, containing no added acid is, for the 2-year aging period, approximately 9 percent. The average loss in tensile strength for a 2-year aging period of 3 lots of straight chesnut-tanned leather previously reported,[4] [5] [6] was approximately 9 percent. This indicates that the large percentage of syntan used in the tanning liquors and the resulting high Procter and Searle value of 1.70 percent had no appreciable influence on the loss in tensile strength of the leather containing no added acid over an aging period of 2 years. The chestnut-syntan leather in lot 28, containing no added acid, showed less than a normal deterioration in strength, and the chestnut-sulphite cellulose leathers in lot 30 were stronger at the end of the 2-year period. The quebracho leathers containing syntan and sulphite cellulose and the sulphited quebracho leathers appear to have aged normally when compared with previous lots of these leathers tanned without the use of sulphur-containing materials. As shown in table 3, in all cases there was a loss in tensile strength immediately after treatment of the samples with acid when compared with the samples treated with water for control. This loss in strength is considered in the final results as a part of the total deterioration.

The results for the deterioration of the leathers for the 2-year aging period as a function of the original pH are given in figures 1 to 3, inclusive. The percentage change in tensile strength has been corrected for the loss in strength of the control samples containing no added acid, so that the points in the graphs represent the deterioration caused by the acid.

[4] J. Am. Leather Chem. Assn. **29**, 623 (1934).
[5] J. Am. Leather Chem. Assn. **30**, 91 (1935).
[6] J. Research NBS **15**, 73 (1935) RP811.

Figure 1 shows the effect of humidity on the deterioration of these samples during storage. The leather stored at 85-percent relative humidity showed a larger percentage loss in tensile strength than

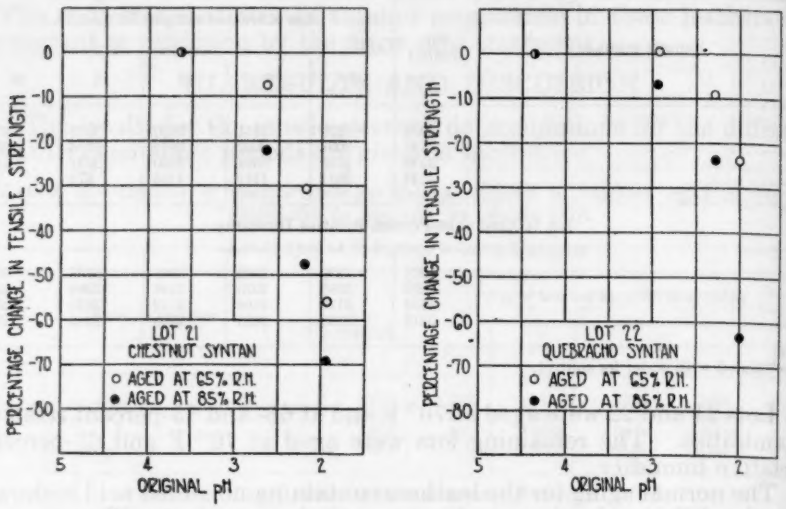


FIGURE 1.—*Effect of* pH *on the change in tensile strength of leathers aged for 2 years.*

similar leathers stored at 65-percent relative humidity. This is particularly noticeable with the leathers having a low pH value.

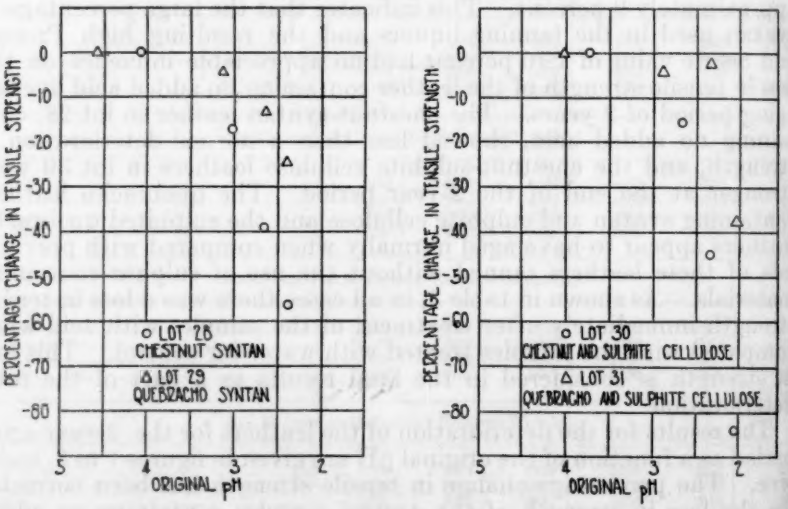


FIGURE 2.—*Effect of* pH *on the change in tensile strength of leathers aged for 2 years.*

The chestnut leathers at the lower pH values show a much greater deterioration than the quebracho leathers at the same pH.

In figure 2, lot 31, the point representing the percentage loss in tensile strength for the quebracho leather having a pH value of 2.3 is

doubtful, probably because of a variation in the uniformity of this group of samples, since it is shown in table 2 that there was a much greater loss in strength for the 18-month period than for the 24-month period.

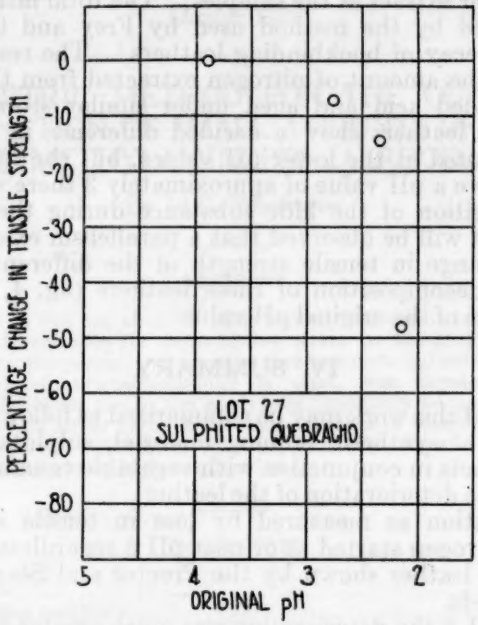
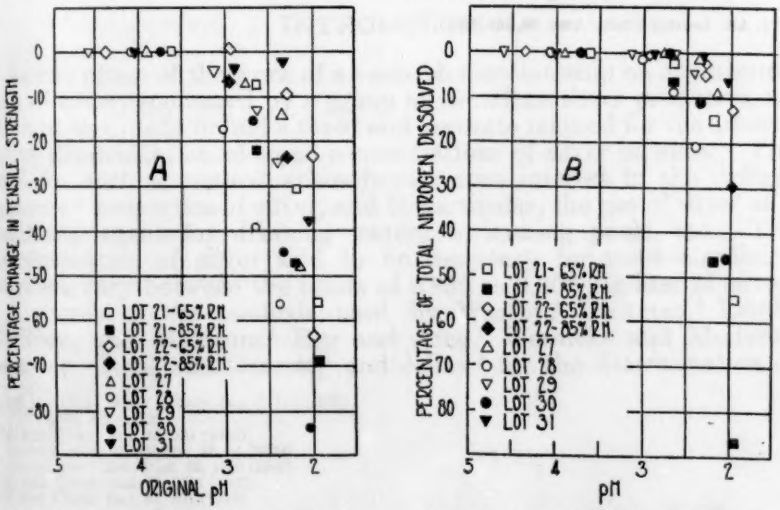


FIGURE 3.—*Effect of* pH *on the change in tensile strength of leather aged for 2 years.*

The results for the 7 lots of leather are shown plotted on the same graph in figure 4. With the exception of 1 lot of leather, the percent-



Graph A.—Effect of pH on the change in tensile strength.

Graph B.—Effect of pH on the total nitrogen dissolved.

FIGURE 4.—*Results for the 7 lots of leather showing physical and chemical deterioration after 2-year aging period, as a function of the original* pH.

age change in tensile strength of the samples having an original pH of 3 or higher, was less than 10 over the 2-year aging period.

The chemical change in the leather, shown by the amount of soluble nitrogen, is also presented in figure 4 as a function of the pH value of a water extract of the samples. The total nitrogen extracted was determined by the method used by Frey and Clarke in their work on the decay of bookbinding leathers.[7] The results have been corrected for the amount of nitrogen extracted from the leather containing no added acid and aged under similar storage conditions. Some of these leathers show a decided difference in the amount of nitrogen extracted at the lower pH values, but the results definitely show that above a pH value of approximately 3 there was no appreciable decomposition of the hide substance during the 2-year period of the test. It will be observed that a parallelism exists between the percentage change in tensile strength of the different leathers, and the chemical decomposition of these leathers (fig. 4, graphs A and B) as a function of the original pH value.

IV. SUMMARY

The results of this work may be summarized as follows:

1. The use of synthetic tanning material, sulphite cellulose, and sulphited extracts in conjunction with vegetable tannins did not cause any appreciable deterioration of the leather.

2. Deterioration as measured by loss in tensile strength or by extractable nitrogen started at or near pH 3 regardless of the amount of acid in the leather shown by the Procter and Searle or the total sulphur methods.

3. Below pH 3 the deterioration was much greater for leathers containing chestnut extract than for leathers containing quebracho extract.

WASHINGTON, August 6, 1935.

[7] J. Am. Leather Chem. Assn. **26**, 461 (1931).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP836

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A COLORIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF SILVER BY USE OF *p*-DIMETHYLAMINOBENZALRHODANINE

By Irl C. Schoonover

ABSTRACT

Recent interest in the use of silver as a bactericidal agent led to the study of analytical methods suitable for determining silver in the small concentrations employed for these purposes. A sensitive and accurate colorimetric method, in which *p*-dimethylaminobenzalrhodanine is used, was developed. Soft-glass dishes are not suitable for use in the analytical procedure because of a very pronounced adsorption of silver on such surfaces. Dishes of fused silica or of Pyrex glass were satisfactory. Chlorides, sulfates, and cupr us and mercurous salts interfere with this colorimetric determination.

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I. INTRODUCTION

As one phase of the work of a research associateship on engineering uses of silver, sponsored by a group of American silver producers, an attempt was made to find a rapid and accurate method for the quantitative determination of small concentrations of silver in water. The need for such a method arises from recent interest in the "oligodynamic" properties of silver, and in particular, the use of silver as a sterilizing agent for drinking waters, swimming pools, etc. The concentrations of silver said to be necessary for most sterilizing purposes vary between the limits of 0.030 to 0.300 mg/liter of silver.

A survey of the methods used by Whitby,[1] Hickman,[2] Lamb, Carleton, and Meldrum,[3] Egg and Jung,[4] Wernicke and Modern,[5] Johnston, Cuta, and Garrett,[6] and Jelley[7] for the determination of

[1] 7th Int. Cong. Appl. Chem. Sec. I, 112 (1909).
[2] Phot. J. **62**, 512 (1922).
[3] J. Am. Chem. Soc. **42**, 251 (1920).
[4] Schweiz. med. Wochschr. **59**, 84 (1929).
[5] Compt. rend. Soc. Biol. **99**, 1519 (1928).
[6] J. Am. Chem. Soc. **55**, 2311 (1933).
[7] J. Soc. Chem. Ind. **51**, 191 (1932).

silver indicated that they are not entirely suited to the present problem, as either a complicated apparatus must be employed or large volumes of water must be evaporated to bring the silver content within the limit of sensitivity of the methods.

Feigl [8] reported a method for the qualitative detection of very small amounts of silver based upon the color produced when an acetone solution of *p*-dimethylaminobenzalrhodanine is added to a nitric-acid solution of silver, claiming a sensitivity of 1 part of silver in 5 million parts of water. Later, Kolthoff [9] confirmed the findings of Feigl and extended the use of the rhodanine compound to the qualitative detection of cuprous copper and mercurous mercury. Ettish and Tamehyna [10] used this compound for the detection of silver and claimed that by their procedure the reagent is sensitive to 1 part of silver in 40 million parts of water.

In the present study, a colorimetric procedure for the quantitative determination of silver by use of this reagent has been developed. Silver may be determined directly, without evaporations, in solutions containing as little as 0.06 mg/liter of silver and up to 9 mg/liter, with an accuracy of 3 percent or better. The more serious complications encountered in this method are the adsorption of silver on the walls of glass containers and the interference of certain elements, particularly chlorides. However, by following certain percautions excellent results may be obtained.

II. MATERIALS AND METHODS

Solutions of silver used as standards in this study were prepared by dissolving weighed portions of pure silver (99.993 percent Ag) in nitric acid, using fused-silica volumetric flasks. A 0.02 percent alcoholic solution of *p*-dimethylaminobenzalrhodanine was the color-producing agent.

Blood-sugar tubes of 20-ml capacity were used in the preliminary experiments in making color comparisons. Later, fused-silica test tubes of 30-ml capacity were used for this purpose.

Volumetric flasks, pipettes, and evaporating dishes made of fused silica were used for the most precise and dependable determinations. Pyrex glass was later proved suitable for handling the silver solutions at room temperatures.

The procedure followed varied but little from that outlined by Feigl,[8] and later by Kolthoff,[9] for the qualitative detection of silver. For the preliminary experiments color tubes used as standards for evaluating the silver content of an unknown solution were prepared by placing portions of a silver-nitrate solution containing 0.001607 g of silver/liter in a series of fused-silica tubes.[11] Each successive tube in a series contained 0.1 ml more of this silver-nitrate solution than the preceding tube. To each tube were then added 0.5 ml of approximately $4N$ HNO_3 solution and sufficient water to make the total volume 15 ml. These solutions were thoroughly mixed, using a clean rubber stopper to close the end of the tube. Then 0.5 ml of a 0.02-percent alcoholic solution of *p*-dimethylaminobenzalrhodanine was added and the contents were again mixed to develop the pink or red color characteristics of the silver-rhodanine solution.

[8] Z. anal. Chem. **74**, 380 (1928).
[9] J. Am. Chem. Soc. **52**, 2222 (1930).
[10] Mikrochemie **10**, 92 (1931).
[11] Pyrex-glass tubes may be substituted for fused silica.

To determine the sensitivity of the color comparisons in ranges of different concentrations of silver, several series of color tubes were prepared representing concentration ranges from 1 to 10 ml of the above-mentioned silver-nitrate solution. The colors developed in these series were observed at 5-minute intervals for a period of 45 minutes. The maximum depth of color developed after 30 minutes, and did not fade on standing for an hour or more. The color varied from a pale pink in the tubes containing the smallest concentration of silver to a deep red in those having the greatest concentration of silver. The differences between any two tubes in a series and also between any single tube and a blank containing no silver were readily recognizable.

In this procedure the concentration of nitric acid, as well as the order in which it is added, is important. The addition of too much acid appreciably decreases the sensitivity of the test, while the addition of the acid following the rhodanine reagent causes the formation of a yellow precipitate, which is not readily soluble and interferes with the color comparisons. In cleaning the tubes after any determination, it was found advisable to rinse them thoroughly with concentrated nitric acid, as there is a tendency for some of the colored silver compound to cling to the walls of the tubes and to impart a slight color.

III. EXPERIMENTAL RESULTS

1. ADSORPTION EFFECTS

Early in this study it was observed that silver was lost when very dilute silver solutions were prepared by repeated dilution in soft-glass volumetric flasks. The losses in some cases amounted to 10 to 20 percent of the silver calculated to be present and varied with the number of determinations made and the nature and previous history of the flasks. Later experiments showed that this loss was due to adsorption of silver on the surface of the flasks.

The adsorption of silver ions from solutions has been reported by a number of investigators. Freundlich and Söllner [12] found a nearly irreversible adsorption of silver from solutions contained in glass and porcelain, but none in fused-silica containers; Horovitz and Zimmermann [13] reported that silver was adsorbed from solutions when in contact with certain types of German resistant glass; Kolthoff [14] studied the adsorption of silver, copper, zinc, and lead on glass wool; Quittner [15] made studies of the migration of ions from aqueous solutions into glass; and Mulligan [16] observed this effect in his work on the electrolysis of soda-lime glass. Haber,[17] in his work on the gold and silver content of sea water, found it to be necessary to employ special procedures to prevent the adsorption of silver and gold on the surface of glass containers.

Since very dilute silver solutions were to be employed in this investigation a further study of this adsorption effect was undertaken. The effect of increased area of contact of the solution with soft-glass surfaces was first considered. Two silver solutions were prepared in soft-glass volumetric flasks, one of which contained 1 ml of a silver-

[12] Biochem. Z. **203**, 3 (1928).
[13] Sitz. Akad. Wiss. Wien [II] **134**, 355 (1925).
[14] Pharm. Weekblad **58**, 463 (1921).
[15] Ann. Physik [IV] **85**, 745 (1928).
[16] Trans. Roy. Soc. Canada [III] **19**, 35 (1925).
[17] Z. angew. Chem. **40**, 303 (1927).

nitrate solution, containing 0.3208 g/liter of silver diluted to 250 ml, and the other contained 2 ml of the same solution diluted to 500 ml (table 1, series A). The concentration of silver in the two flasks was, therefore, the same, but there was a greater ratio of soft-glass surface to volume of solution in the smaller flask. Greater loss of silver resulted from the dilution in the 250-ml flask, as was shown by comparing the colors developed in pairs of tubes containing in one tube of each pair a definite volume of the silver solution from the 250-ml flask and in the other tube the same volume of solution from the 500-ml flask. This result is consistent with the conception that adsorption should be more pronounced in the flask having the greater ratio of surface area to volume of solution; that is, in the 250-ml flask.

TABLE 1.—*Losses of silver from dilute silver-nitrate solutions through adsorption*

Series	Experiment	Concentration of silver in original solution	Volume of original solution taken for dilution	Volume of diluted solution	Type of container used for dilution	Volume of diluted solution used	Silver content		Error	Footnote
							Calculated	Found		
		g/liter	ml	ml		ml	mg	mg	Percent	
	------	0.3208	2	500	Soft-glass flask (500 ml).	4	[a] 0.0051	----------	----------	
	------	.3208	2	500		5	[a] .0064	----------	----------	
A	1	.3208	1	250	Soft-glass flask (250 ml).	4	.0051	<0.0051	Loss	
	2	.3208	1	250		5	.0064	<.0064	do	
	------	.3208	4	1,000	Silica flask (1,000 ml).	2	[a] .0026	----------	----------	
	------	.3208	4	1,000		3	[a] .0038	----------	----------	
	------	.3208	4	1,000		4	[a] .0051	----------	----------	
A_1	21	.3208	2	500	Silica flask (500 ml).	2	.0026	.0026	None	
	22	.3208	2	500		3	.0038	.0038	do	
	23	.3208	2	500		4	.0051	.0051	do	
	------	.3208	2	500		2	[a] .0026	----------	----------	
	------	.3208	2	500		4	[a] .0051	----------	----------	
	------	.3208	2	500		5	[a] .0064	----------	----------	
B	3	.3208	2	500	Soft-glass flask (500 ml).	2	.0026	<.0026	Loss	
	4	.3208	2	500		4	.0051	<.0026	do	[d]
	5	.3208	2	500		6	.0064	<.0026	do	
	------	.3208	2	500		3	[a] .0038	----------	----------	
	------	.3208	2	500		4	[a] .0051	----------	----------	
	------	.3208	2	500		5	[a] .0064	----------	----------	
	------	.3208	2	500		2	[a] .0026	----------	----------	
	13	.3208	2	500	do	4	.0051	.0038	−25	[e]
C	14	.3208	2	500		5	.0064	.0051	−20	
	15	.3208	2	500		3	.0038	<.0026	Loss	
	16	.3208	2	500		4	.0051	<.0026	do	[e]
	17	.3208	2	500		5	.0064	<.0026	do	
	18	.3208	5	1,000	Soft-glass flask (1,000 ml).	3	.0048	<.0026	do	
	19	.3208	5	1,000		4	.0064	<.0026	do	[f]
	20	.3208	5	1,000		5	.0060	<.0038	do	
	------	.3208	2	500	Silica dish (500 ml).	4	[a] .0026	----------	----------	
	------	.3208	2	500		5	[a] .0064	----------	----------	
D	6	.3208	2	500	Soft-glass flask (500 ml).	4	.0051	.0018	−65	
	7	.3208	2	500		5	.0064	.0030	−53	
	------	.2959	1	500		4	[a] .0024	----------	----------	
	------	.2959	1	500		5	[a] .00295	----------	----------	
	------	.2959	1	500		6	[a] .0035	----------	----------	
	------	.2959	1	500		7	[a] .0041	----------	----------	
E	8	.0963	1	500	do	15	.0028	.0028	0	[g]
	9	.0963	1	500		20	.0038	.0036	−5	
	10	.0963	1	500		20	.0038	.0040	+5	
	11	.0963	1	500		15	.0028	<.0024	Loss	[c]
	12	.0963	1	500		20	.0024	<.0024	do	

[a] Arbitrarily taken as a standard and assumed to have no adsorption losses.
[b] Evaporation of the 15- and 20-ml portions of silver solution was made in fused-silica dishes.
[c] Evaporation of the 15- and 20-ml portions of silver solution was made in Pyrex-glass beakers.
[d] 200 g of untreated soft-glass beads were added to the solution.
[e] 200 g of soft-glass beads previously treated in a 25-percent NaOH solution were added.
[f] 200 g of broken Pyrex-glass beakers were added.
[g] 200 g of soft-glass beads previously treated in dichromate cleaning solution were added.

The same experiment was repeated later by using 1,000- and 500-ml silica flasks instead of soft-glass flasks. In this case, a comparison of the color in one tube of each pair, containing a definite volume of silver solution from the 500-ml flask, with that in the second tube, containing the same volume of solution from the 1,000-ml flask, showed that there was no loss of silver (see section A_1 of table 1).

Further experiments were made in which the surface area exposed to the solution was increased by the addition of soft-glass beads (table 1, series B). A rhodanine color series was prepared from a dilute silver solution (0.00128 g Ag/liter) contained in a 500-ml soft-glass volumetric flask. A portion of this solution was then removed and approximately 200 g of soft-glass beads, which previously had been cleaned and dried, were added to the remainder of this solution. After the solution containing the beads was shaken thoroughly, and let stand for ½ hour, a rhodanine color series was prepared from this solution and compared with a color series made from that portion of the solution which was removed before the addition of the beads. Large differences in color were again obtained for those portions not containing the glass beads and those with the glass beads, the difference amounting to as much as approximately 50 percent.

The amount of silver adsorbed on the beads varied, depending upon their previous treatment. Beads that stood in a dichromate cleaning solution overnight and then were thoroughly rinsed with water and dried, adsorbed less silver than a similar quantity of beads which had been kept in a 25-percent sodium-hydroxide solution for the same length of time (table 1, series C—experiments 13 and 14 and 15 to 17). No determinations were made to ascertain whether these differences in color were due to a change in the surface of the beads, due to adsorbed alkali, or to a slight amount of sulphuric acid from the dichromate cleaning solution which might not have been removed from the surface by repeated washing. Sulphuric acid was subsequently found to increase the depth of the rhodanine color.

Similar trials of increased adsorption resulting from the larger amount of glass surface exposed to the solution were made, using approximately 200 g of broken Pyrex glass in one case (table 1, series C; experiments 18 to 20), and the same weight of broken soft glass in the other. The results were similar to those obtained when glass beads were used, with the exception that broken Pyrex glass adsorbed less silver than broken soft glass.

Further experiments on the adsorption of silver on the walls of silica containers were made by diluting 2-ml portions of the silver-nitrate solution to 500 ml in a silica dish and in a soft-glass volumetric flask (table 1, series D). A comparison of the colors in the rhodanine color tubes made from these dilute solutions showed a very large loss of silver in the solution made up in the soft glass; that is, there was, at the most, much less adsorption by the silica container.

Kolthoff [18] reported that the adsorption of silver on glass wool is increased with a rise in temperature of the silver solution. A similar

[18] Pharm. Weekblad 58, 463 (1921).

effect was observed in the present study in that larger losses of silver were observed when attempts were made to concentrate a dilute silver solution by evaporation in Pyrex-glass beakers. On the other hand, evaporation in fused-silica dishes produced little or no losses (table 1, series E). It may be assumed that there is also very little or no adsorption on silica at room temperature.

The data secured thus far indicate that: (a) Soft glass was quite unsuitable for use at any point in handling the silver solutions in determining silver in the concentrations in question; (b) Pyrex glass had less adsorptive power toward silver than soft glass at room temperatures, but should not be used for evaporation of very dilute silver solutions; and (c) fused-silica ware had little or no adsorptive power for silver during evaporation of dilute silver solutions and probably was also free from serious adsorption of silver at ordinary room temperatures. The adsorption of silver was increased when alkali was used for treating soft-glass surfaces, but it was decreased when the alkali was replaced by acid dichromate cleaning solution.

2. ACCURACY AND SENSITIVITY OF METHOD

Solutions for rhodanine color tubes, used in the determination of the accuracy and sensitivity of the method, were prepared and handled throughout in fused-silica ware, such as volumetric flasks, pipettes, and color tubes. It was assumed that by using silica glass there was no serious adsorption of silver from the solutions during any stage of the procedure.

TABLE 2.—*Colorimetric determination of silver*

Experiment	Volume of dilute silver solution	Silver content		Error	Type of flask used for dilution
		Calculated	Found		
	ml	mg	mg	*Percent*	
1	2	0.00107	0.00107	0.0	Pyrex glass.
2	4	.00214	.00214	.0	Do.
3	6	.00321	.00332	+3.4	Do.
4	2	.00107	<.00107	(c)	Soft glass.
5	4	.00214	.00193	−9.8	Do.
6	6	.00321	.00289	−9.9	Do.
7 [a]	4	.00219	.00214	−2.3	Pyrex glass.
8 [a]	6	.00329	.00332	+0.9	Do.
9 [a]	3	.00454	.00450	−0.9	Do.
10 [a]	3	.00454	.00442	−2.6	Do.
11 [a]	12	.00482	.00482	0.0	Do.
12 [a]	12	.00482	.00466	−3.3	Do.
13	4.5	.00681	.00675	−0.9	Do.
14	4.8	.00726	.00723	−0.4	Do.
15	5.0	.00757	.00771	+1.9	Do.
16	[b] 12	.00482	.00487	0.0	Do.
17	[b] 12	.00482	.00466	−3.3	Do.
18	[b] 12	.00482	.00498	+3.2	Do.

[a] The silver content of the solution was not known before test.
[b] After being diluted to 50 ml, the silver solutions were evaporated in fused-silica dishes to about 5 ml, transferred to color tubes, and treated to produce the rhodanine color.
[c] Not determined.

It was found that silver solutions made by diluting in soft-glass volumetric flasks had lost appreciable quantities of silver as judged by comparing with color standards prepared entirely in silica glass (table 2, experiments 4 to 6). On the other hand, silver solutions diluted in Pyrex-glass volumetric flasks showed no loss of silver when compared with the same standards (table 2, experiments 1 to 3). This is in agreement with Horovitz and Zimmerman's results.[19]

The results obtained with various dilute solutions, the concentrations of which were not known previous to test, are given in table 2, experiments 7 to 12. These and all solutions made subsequently were prepared in Pyrex-glass volumetric flasks. The accuracy of the method, as indicated by the results obtained for experiments 7 to 18 of table 2, was ± 3 percent of the quantity of silver determined in solutions of concentrations ranging from 1 to 8 mg/liter of silver. Further, no appreciable loss of silver occurred when the dilution and evaporation of the solution were carried out in fused-silica dishes, as the results for experiments 16 to 18 of table 2 will show.

It was also observed that the color comparisons could be made most easily where the concentration of the solution was between 1 and 6 mg/liter of silver.

IV. FACTORS WHICH MAY INTERFERE WITH THE RELIABILITY OF THE METHOD

Chlorides present in very small amounts in the solution decrease appreciably the sensitivity and accuracy of the rhodanine reagent for silver. The chlorides cause a fading of the color, and consequently low results for silver content are produced. This difficulty may be overcome by repeated evaporations of the solution to dryness with concentrated nitric acid. Definite amounts of chlorides ranging between 10 and 65 g/liter were effectively removed by two evaporations with 20-ml portions of concentrated nitric acid.

Acetic acid, acetone, formaldehyde, ether, alcohol, and ethyl acetate react with the rhodanine reagent to give colors.

Ammoniacal solutions of silver react with the rhodanine reagent to give colors similar to those produced in nitric acid. Greater amounts of silver, however, are required to produce the same depth of color in these solutions.

Kolthoff [20] reported that cuprous copper and mercurous mercury react with rhodanine to give colors similar to those produced by silver.

Calcium carbonate in amounts less than 1 mg/liter has no effect on the rhodanine color, though the color is deepened if the quantity of the carbonate exceeds this value.

Sodium nitrate has no effect on the depth of the rhodanine color if it is present in amounts less than 1 mg/liter but greater amounts of this salt increase the depth of the rhodanine color. Ammonium nitrate decreases the sensitivity of the test if in amounts as much as 0.6 mg/liter.

Very small amounts of either sulphuric acid or potassium sulphate (0.6 g/liter for the latter) increase the depth of the rhodanine color.

[19] Sitz. Akad. Wiss. Wien. [Ü] **134**, 355 (1925).
[20] Pharm. Weekblad **58**, 463(1921).

V. SUMMARY

A sensitive method for the colorimetric determination of silver, using *p*-dimethylaminobenzalrhodanine, has been developed.

The adsorption of silver from dilute solutions is appreciable on soft glass, slight on Pyrex glass at room temperature, and negligible on fused silica. Therefore, soft-glass containers should not be employed in the procedure.

The sensitivity and accuracy of the colorimetric test may be impaired if the quantities of certain substances exceed definite values. Notable among the inorganic substances thus interfering are chlorides, sulfates, and cuprous and mercurous salts.

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HARDENING CHARACTERISTICS AND OTHER PROPERTIES OF COMMERCIAL ONE-PERCENT-CARBON TOOL STEELS

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ABSTRACT

Widely used brands of 1-percent-carbon tool steels produced by one foreign and five domestic manufacturers were classified on the basis of their depths of hardening. Two of these steels, having widely different hardening characteristics, were selected for a study of the effect of initial structure on the austenitic grain size and grain growth and on the critical cooling rates. These data made possible a direct comparison of the relation between austenitic grain size and critical cooling rates over a range of quenching temperatures of 1,425 to 1,775° F. Comparisons of the two steels were also made with respect to their behavior in the transformation temperature range during thermal analysis, relative rates of spheroidization, Charpy impact strengths, relative susceptibility to grinding cracks, hardness values on quenching with different rates, structural normality, performance as lathe tools and the effect of rate of heating to the hardening temperatures on depth of hardening.

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I. INTRODUCTION

Plain carbon tool steels of apparently the same composition often have widely different hardening characteristics. This important fact has been recognized for many years but definite progress in explaining the fundamental causes of this difference in behavior has been made only in the last decade. Recent investigations have at least partially explained this anomaly by showing the marked influence exerted by the austenitic grain size on the hardenability of steel.

The influence of initial structure (structure prior to hardening) upon the austenitic grain size and hence upon hardenability was also recognized by those most active in developing the theories of effects of grain size. This factor has, however, received less attention than many other phases of austenitic grain-size influence.

The experiments described in this report were made in the course of a study of the hardening characteristics of commercial 1-percent-carbon tool steels. Particular attention was given to the influence of initial structure of two selected steels (which had wide differences in their depth of hardening) upon the grain size and grain growth of their austenite in and above the usual range of hardening temperatures, and upon the critical cooling rates on quenching from a similar range of temperatures. Comparisons of these two steels were also made with respect to their behavior in the transformation temperature range during thermal analysis, relative rates of spheroidization, Charpy impact strengths, relative susceptibility to grinding cracks, Rockwell hardness values on quenching with different rates, structural normality, performance as lathe tools, and the effect of rate of heating to the hardening temperatures on the depth of hardening.

II. PREVIOUS INVESTIGATIONS

In 1922 McQuaid and Ehn [1] reported a difference in the hardening of carburized plain carbon steels. The ability to harden was related to the "normal" or "abnormal" structure of the steel. In the shallow-hardening or abnormal steel the grain size was usually small and, on slow cooling from the carburizing temperature, the cementite in the hypereutectoid zone existed as coalesced masses generally surrounded by ferrite. In the relatively deep-hardening or normal steel, the grain size was large and the pearlite grains in the hypereutectoid zone were inclosed by thin films of cementite. Abnormality was believed to be caused by oxides, either in solution or as submicroscopic particles.

Epstein and Rawdon [2] pointed out that abnormality in commercial carburizing steels seemed, in most cases, to be associated with the use of aluminum for deoxidizing and that the higher carbon tool steels had features of normality and abnormality similar to those met in carburizing steels.

Davenport and Bain [3] considered that the structure and hardness in a quenched steel depend primarily on the particular temperature at which austenite decomposes during the quenching. The rate at which the steel cools during the quenching is important only in determining to how low a temperature austenite can be cooled before its decomposition begins. They concluded that hardenability of a steel depends upon the stability of quenched austenite in the temperature range of 1,110 to 930° F, the upper range in which austenite is most prone to decompose and in which its decomposition products are relatively soft. If the austenite of a steel is relatively stable in this temperature range and can be cooled through this range by a mild quench, then it decomposes only in the range below about 300° F, the product of decomposition is martensite, and the steel is

[1] W. H. McQuaid and E. W. Ehn, Trans. Am. Inst. Min. Met. Engrs. **67**, 341–391 (1922).
[2] S. Epstein and H. S. Rawdon, BS J. Research 1, 423–466 (1928) RP14.
[3] E. S. Davenport and E. C. Bain, Trans. Am. Inst. Min. Met. Engrs., Iron & Steel Div. **90**, 117–154 (1930).

fully hardened. Such a steel may, therefore, be called a "deep-hardening" steel as compared with another in which the austenite is less stable in the range, 1,110 to 930° F, and which, therefore, does not fully harden under identical quenching conditions.

Bain [4] further clarified the conception of hardenability by suggesting that the factors which determine the relative stability of austenite in the temperature range, 1,110 to 930° F, are (1) its chemical composition and (2) its grain size.

The far-reaching effect of austenitic grain size and its control has been discussed in a number of recent papers, notably those of the "Grain Size Symposium" of the American Society for Metals.[5]

In papers presented before the American Society for Steel Treating in 1929, both Shepherd and Luerssen discussed variations in the hardenability of tool steel. Shepherd [6] described a simple test for depth of hardness and Luerssen [7] pointed out the desirability, as well as the possibility, of controlling melting conditions to produce carbon tool steel with a predetermined hardness penetration and quenching temperature range. Such tool steels were shortly made available commercially.

Harrington [8] studied the effect of initial structure on the "body" (that is, the ability to withstand repeated heating and cooling cycles), the hardness, and the structure of hardened 1- percent-carbon tool steel. The body of the steel was influenced by the initial structure with quenching temperatures of 1,380 or 1,470° F, but was not affected when the quenching temperature was increased to 1,650° F.

Tests to determine the effect of various amounts of spheroidized cementite in the initial structure on the hardness of quenched specimens of a 0.9- percent-carbon steel have been reported by Lljynski.[9] Increasing the amount of spheroidized cementite in the initial structure resulted in a decrease in the hardness of the quenched steel.

In 1933 Engel and Engel [10] reported the results of their investigation on the effect of initial structure on the critical cooling rate of a 1-percent-carbon steel. Microscopical examination was made of specimens with different initial structures that were heated for varying lengths of time, quenched, and fractured. However, actual cooling rates and the austenite grain-size determinations, are not included in their published data.

Shepherd [11] recently called attention to the dependence of "penetration-fracture characteristics" of tool steel on the heat treatment and the microstructure of the steel prior to heating for hardening.

III. STEELS STUDIED

Plain carbon tool steels, of about 1-percent carbon representing widely used brands, were purchased through regular channels of supply from one foreign and five domestic manufacturers. Tests for the depth of hardening were made on initially spheroidized specimens by quenching ¾-inch rounds in brine from two temperatures,

[4] E. C. Bain, Trans. Am. Soc. Steel Treating **20**, 385–428 (Nov. 1932).
[5] Trans. Am. Soc. for Metals **22** (Dec. 1934).
[6] B. F. Shepherd, Trans. Am. Soc. Steel Treating **17**, 90–110 (Jan. 1930).
[7] G. V. Luerssen, Trans. Am. Soc. Steel Treating **17**, 161–198 (Feb. 1930).
[8] R. H. Harrington, Trans. Am. Soc. Steel Treating **18**, 404–422 (1930).
[9] S. K. Lljynski, Proc. Second Congress of Scientific Promoters of Metallurgy in Leningrad, 161 (May 1924); Abs., Trans. Am. Soc. Steel Treating **9**, 492 (1926).
[10] W. Engel and N. Engel, Jernkontorets Ann. **117**, 409–418 (August 1933).
[11] B. F. Shepherd, Trans. Am. Soc. for Metals **22**, 979–1,016 (Dec. 1934).

1,425 and 1,550° F, and etching a section to show the hardness penetration. On the basis of these tests two steels were selected which had very similar depth of hardening on quenching from 1,425° F (within the usual hardening range), but very different depths of hardening on quenching from 1,550° F. The hardened and etched sections of these steels are shown in figure 1. Steel 65 obviously has markedly changed in its depth of hardening as a result of increasing the quenching temperature from 1,425 to 1,550° F, while steel 68 has changed very little. Steel 68 was, in fact, produced under conditions which resulted in control of austenitic grain size and was marketed with specific claims as to its uniformity in depth of hardening by quenching within and above the usual quenching temperature ranges. In this paper these two steels are occasionally indicated by the terms "shallow-hardening" or "controlled" for steel 68 and "deep-hardening" or "noncontrolled" for steel 65. As shown in table 1, the chemical compositions of the two steels differed chiefly in the aluminum and aluminum oxide contents. The controlled steel (68) contained appreciably greater proportions of both metallic aluminum (that portion soluble in acid) and aluminum oxide than the noncontrolled steel (65). The steels would be expected to have quite similar hardening characteristics if chemical composition were the only basis of comparison.

TABLE 1.—*Chemical composition of steels with different hardening characteristics*

Steel identification number	Chemical composition (percent by weight)															
	C	Mn	P	S	Si	Cr	Ni	W	Mo	V	Al_2O_3	Acid soluble Al	Total Al	H	O	N
65	1.05	0.28	0.019	0.013	0.22	0.08	0.13	(1)	<0.01	<0.01	0.006	0.001	0.004	0.0002	0.007	0.009
68	1.06	.26	.013	.011	.19	.09	.10	(1)	<.01	<.01	.010	.008	.013	.0003	.009	.007

[1] Not detected.

IV. COMPARISON OF DEEP-HARDENING AND SHALLOW-HARDENING STEELS

1. THERMAL ANALYSIS

Heating and cooling curves were made on specimens of steels 65 and 68, which were initially either normalized to produce a structure consisting essentially of lamellar pearlite or annealed to spheroidize the cementite. The curves were obtained on approximately ¼- by ½- by ⅜-inch specimens heated and cooled in vacuum at a rate of 14 to 18° F per minute.

Typical inverse-rate and time-temperature curves for initially normalized samples are reproduced in figures 2 and 3, respectively. Differences were observed in the temperatures for the beginning of the transformation on slow heating and in the behavior of the two steels during this transformation. These effects are shown by the locations, lengths, and widths of the cusps of the heating curves in figure 2. The controlled steel (68) had a narrow transformation range on heating either the initially normalized or the annealed specimens as compared with the noncontrolled steel (65). The nor-

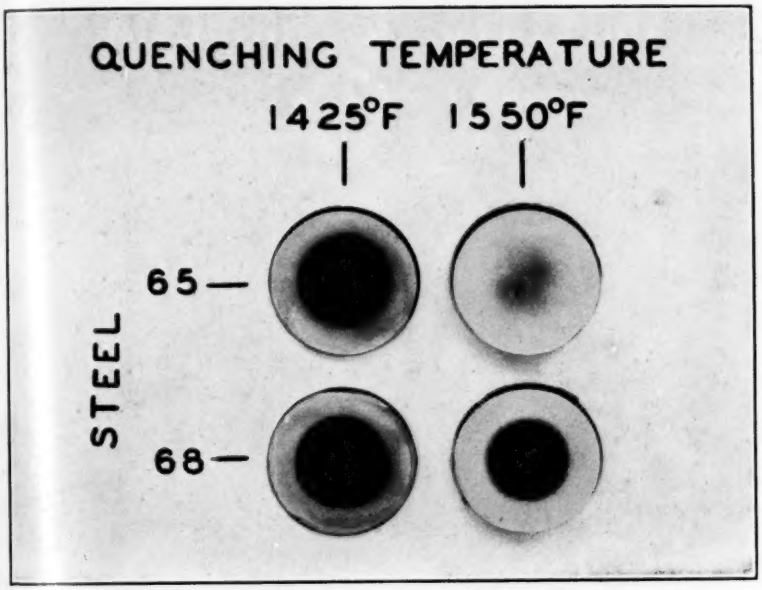

FIGURE 1.—*Relative depth of hardening of steels 65 and 68.*

Initially spheroidized, three-quarter-inch round specimens quenched from 1,425° or 1,550° F. in brine. Etched in 1 percent nitric acid in alcohol to darken the unhardened portions.

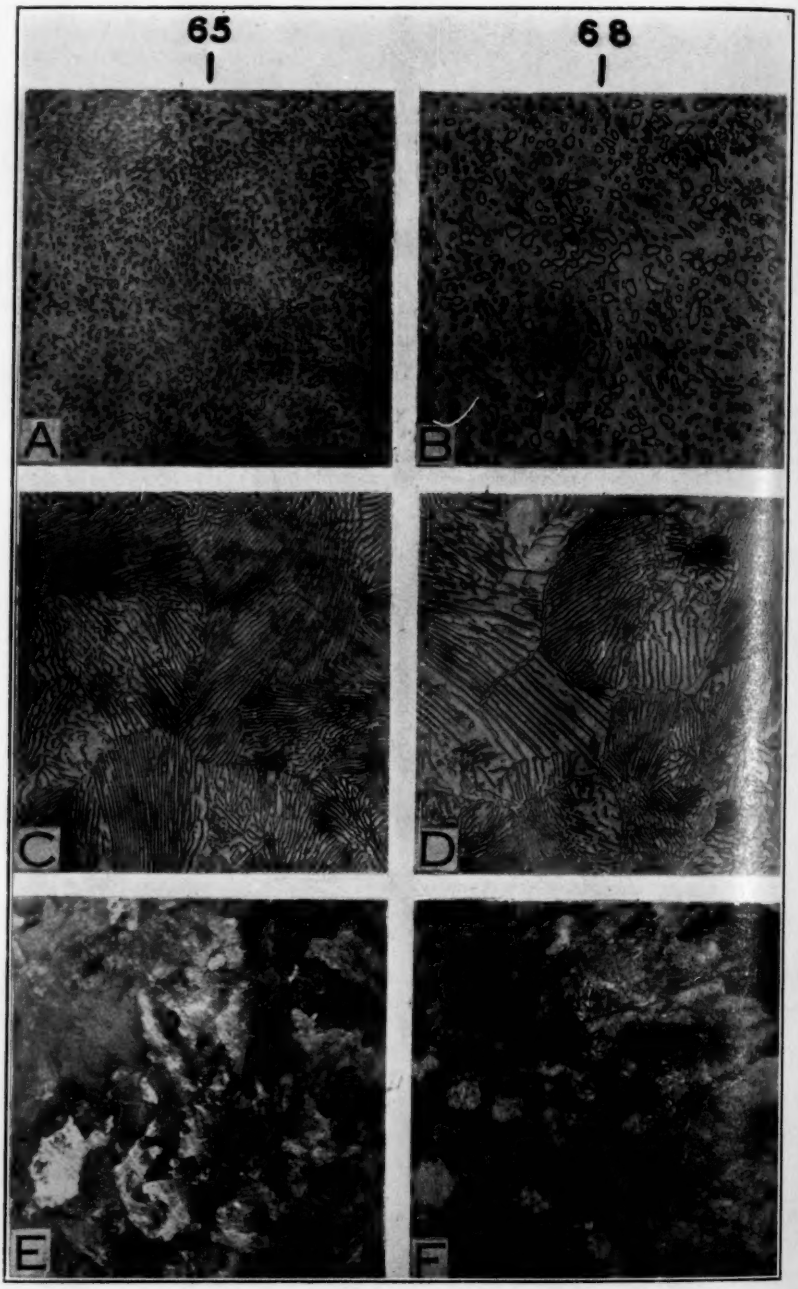

FIGURE 4.—*Initial structure of steels 65 and 68.*

A and *B*, Spheroidized cementite; *C* and *D*, coarse lamellar pearlite; *E* and *F*, sorbite. Etched with 1 percent nitric acid in alcohol, × 500.

malized specimens of steel 68 also had a greater undercooling effect after this transformation once started (fig. 3), than did similarly

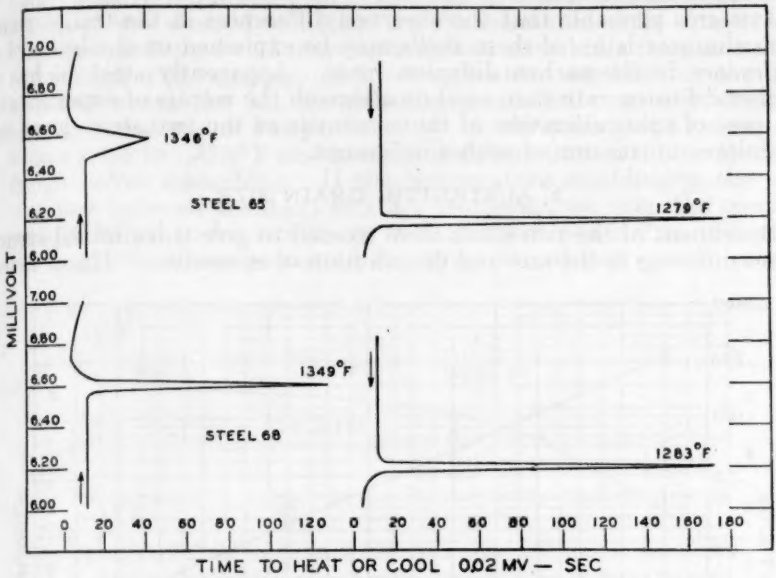

FIGURE 2.—*Inverse-rate heating and cooling curves for steels 65 and 68, with an initial structure of lamellar pearlite.*

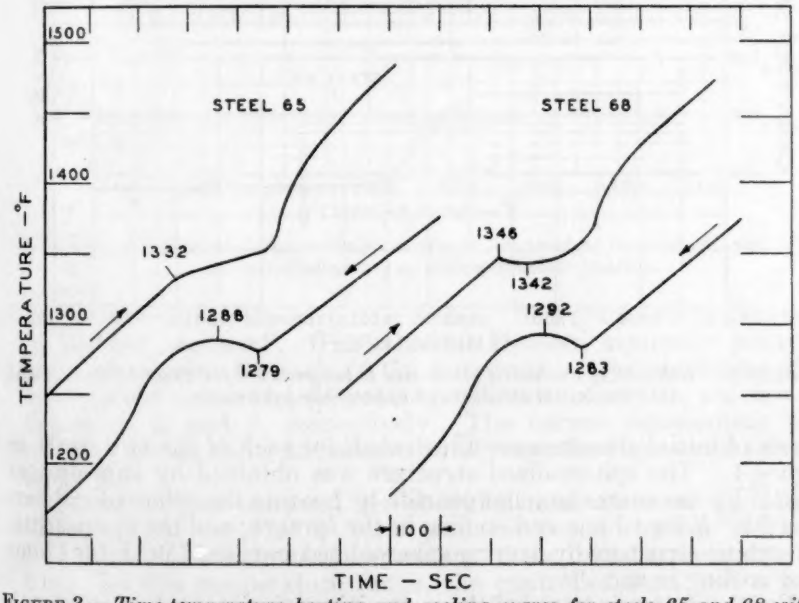

FIGURE 3.—*Time-temperature heating and cooling curves for steels 65 and 68 with an initial structure of lamellar pearlite.*

treated specimens of steel 65. Both steels had similar cooling characteristics on slow cooling from the austenitic condition (1,650 to 1,600° F) at the rate of 14 to 18° F per minute.

The initial structures investigated had no marked influence on the transformation characteristics on comparatively slow heating and cooling of these steels.

It seems probable that the observed differences in the transformation characteristics of these steels may be explained on the basis of a difference in the carbon diffusion rates. Apparently steel 68 has a higher diffusion rate than steel 65 although the results of experiments on rate of spheroidization of the cementite of the two steels gave no definite confirmation of such a difference.

2. AUSTENITIC GRAIN SIZE

Specimens of the two steels were treated to give three initial structures differing in the size and distribution of cementite. These three

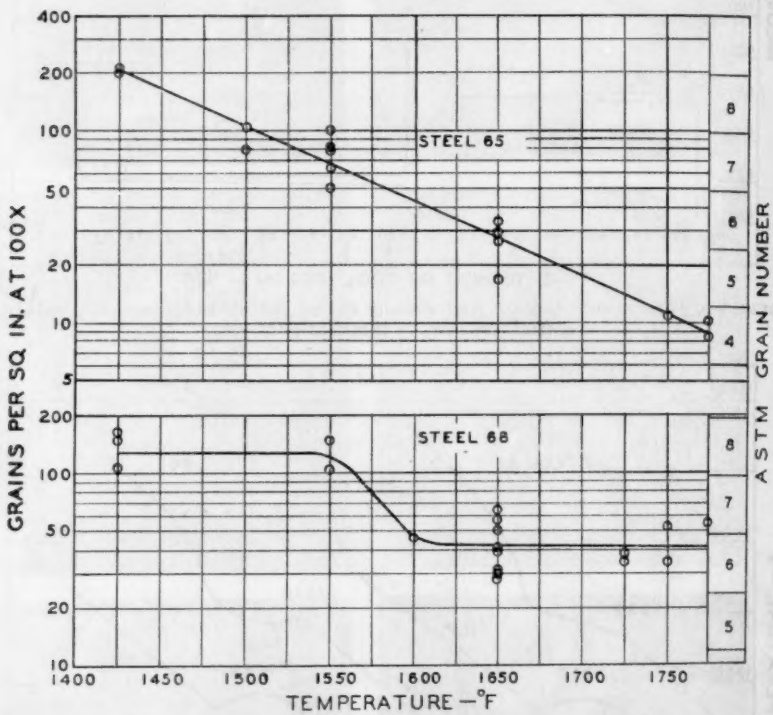

FIGURE 5.—*Relation of austenitic grain size to temperature for steels 65 and 68 with an initial structure of spheroidized cementite.*

types of initial structure are illustrated, for each of the two steels, in figure 4. The spheroidized structure was obtained by annealing at 1,425° F; the coarse lamellar pearlite by heating the spheroidized bars at 1,750° F for 1 hour and cooling in the furnace; and the fine pearlitic or sorbitic structure by heating spheroidized bars to 1750° F for 1 hour and cooling in air.

For the determinations of the austenitic grain size and grain growth specimens ¼-inch square by 0.040-inch thick were cut from the ¾-inch rounds of both steels having each of the three initial structures. One wire of a 22-gage chromel-alumel thermocouple was spot-welded

to the center of each of the two flat faces of each specimen. The specimens were heated in an atmosphere of dry nitrogen at a rapid rate, usually requiring 1 to 2 minutes to reach the temperature at which it was desired to determine the austenitic grain size, held at that temperature for 15 minutes and then cooled in a manner suitable for outlining the grains. If the temperature establishing the grain size was above the A_{cm} temperature, a cementite network outlining the austenite grains was produced by slowly cooling the specimen to about 1,400 to 1,375° F and holding it a short time in this temperature range before quenching. If the temperature establishing the grain size was between the $A_{3\text{-}2\text{-}1}$ and A_{cm} temperatures, then the specimen was quenched under conditions (i. e., slightly slower than the critical cooling rate) which permitted the formation of just enough primary

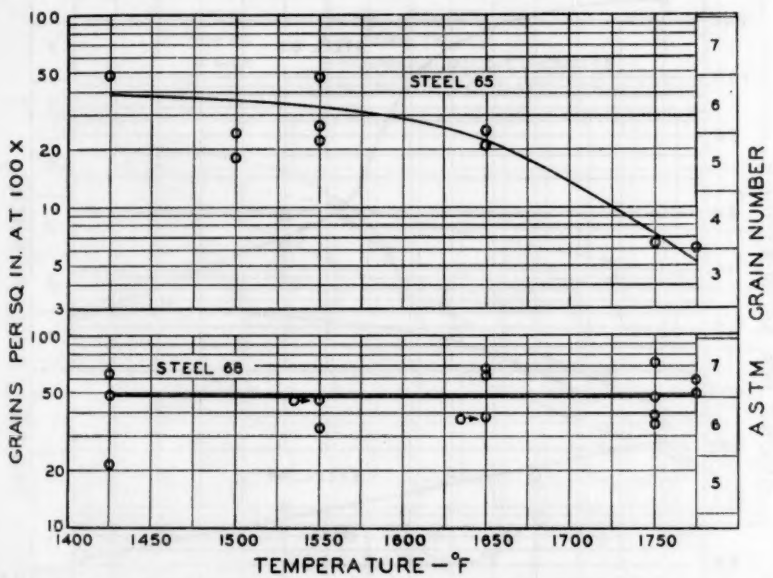

FIGURE 6.—*Relation of austenitic grain size to temperature for steels 65 and 68 with an initial structure of coarse lamellar pearlite.*

troostite to outline the austenitic grains. The grain counts were made by Jeffries' method [12]. The relations between austenitic grain size and temperature for each of the initial structures consisting of (a) spheroidized cementite, (b) coarse pearlite or (c) sorbite, are shown in figures 5, 6, and 7, respectively. The curves representing these relations for all three initial structural conditions are summarized in figure 8.

At the highest temperatures at which measurements were made, namely, 1,750 to 1,775° F, each steel developed a rather characteristic grain size which was independent of the initial structural condition. In this temperature range, the controlled steel had a grain-size number of 6 to 7 and the noncontrolled steel of 3 to 4. The grain size versus temperature curves separate into two characteristic groups only at temperatures above 1,600° F, that is, above the

[12] Zay Jefferies, Am. Soc., Testing Materials, Stds. pt. 1, 902 (note 2) (1933).

temperature of the A_{cm} line and in the range in which all cementite is presumably in solution in the austenite. At temperatures from 1,425 to 1,600° F, the range in which the structure consists of austenite and cementite, the grain size is noticeably dependent on the initial structure as well as on the temperature. The noncontrolled steel 65, which is characteristically coarse grained at 1,750° F, had a very fine grain at 1,425° F, if its initial structure prior to heating was either spheroidized or sorbitic. Each steel, with an initially spheroidized or sorbitic structure, had a smaller grain size at 1,425° F than did the same steel with an initial coarse pearlitic structure. The two steels possessed austenitic grain sizes of the same order of magnitude at

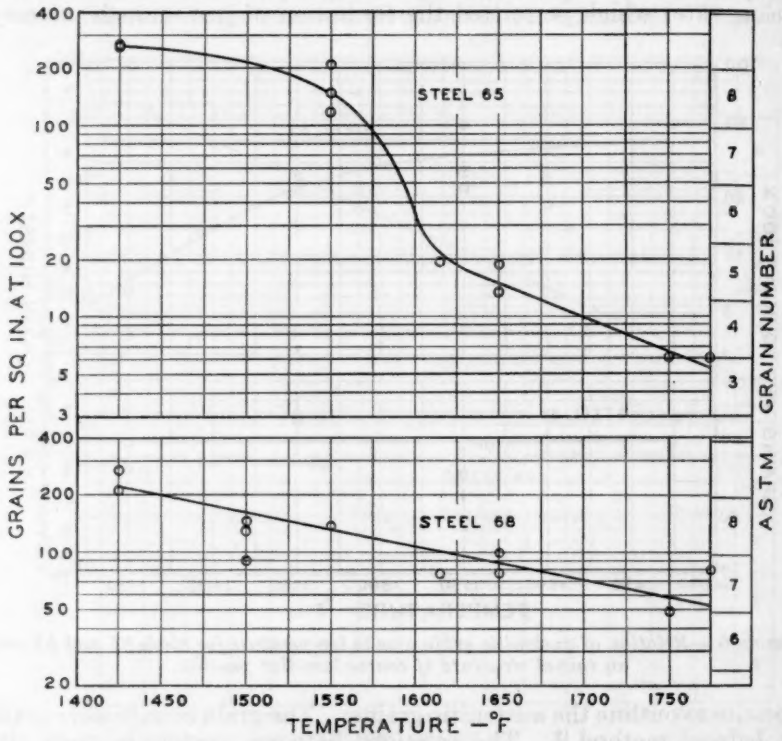

FIGURE 7.—*Relation of austenitic grain size to temperature for steels 65 and 68 with an initial structure of sorbite.*

1,425° F if they had similar initial structures. In two cases sharp inflections occurred in the grain-size-temperature curves, in the temperature range 1,550 to 1,600° F. These inflections evidently indicated the completion of the solution of the separate carbide phase.

These results are consistent with the hypothesis that the greater the degree of subdivision of cementite the smaller the austenitic grain size on heating into the temperature range just above the eutectoid temperature. At 1,425° F in both steels the smallest grain was obtained from the initial sorbitic structure, a slightly larger grain from the spheroidized structure and a relatively coarse grain from the coarse lamellar pearlitic structure. Because each steel ultimately

reached a definite characteristic grain size at the maximum temperature, as is shown in figure 8, it follows that, for a given steel, the initial (prehardening) structure which results in the smallest austenitic grain size (e. g., at 1,425° F) also undergoes the greatest grain growth at the higher temperatures. Whether this subsequent growth takes place steadily and progressively with increasing temperatures or occurs as a more rapid growth over a restricted range of temperature does not appear to be determined by the initial structure. Thus, in the noncontrolled steel (65) rapid growth over a restricted temperature range occurred only in the specimens where initial structure was sorbitic. A similar rapid growth over a small range of temperature occurred only in the spheroidized samples of the controlled steel (68).

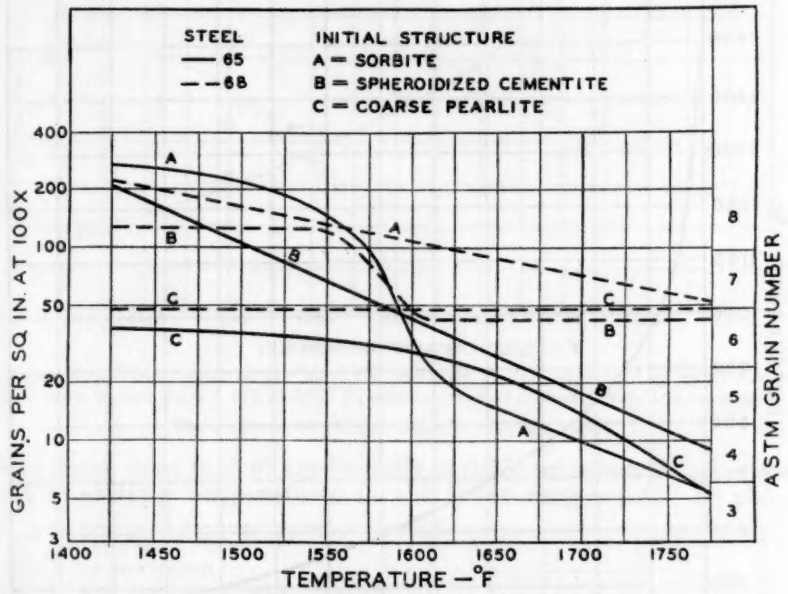

FIGURE 8.—*Relation of austenitic grain size to temperature for steels 65 and 68 with different initial structures.*

3. CRITICAL COOLING RATES

The critical cooling rates were determined for specimens representing the entire range of austenitic grain sizes developed in each steel from each of the three initial structures. The critical cooling rate was taken as the average cooling rate between 1,110 and 930° F when the structure of the quenched specimen was martensite containing nodular troostite in proportions estimated to be between 1 and 3 percent. The specimens for the determinations of the critical cooling rates were of the same shape and size as those used for the determination of the grain size and were heated in the same manner, held for the same time at the temperature establishing the austenitic grain size, and were then quenched directly from that temperature into a suitable quenching medium contained in a bath which sealed the bottom end of the vertical tube of the heating furnace. A photographic time-temperature curve was obtained during the quench in the manner previously

described by French and Klopsch.[13] Examination of the microstructure of the quenched specimens was made on a cross-section of the 0.040-inch-thick sheet near the point of contact of the thermocouple wires. A typical time-temperature cooling curve plotted from the data obtained from a photographic record is shown in figure 9.

The relations between the time required to cool from 1,110 to 930° F and the quenching temperature (which was also the temperature establishing the austenitic grain size) for the initially spheroidized specimens of steels 65 and 68 are shown in figures 10 and 11, respectively, for the initially coarse pearlitic specimens in figures 12 and 13, respectively, and for the initially sorbitic specimens in figures 14 and 15,

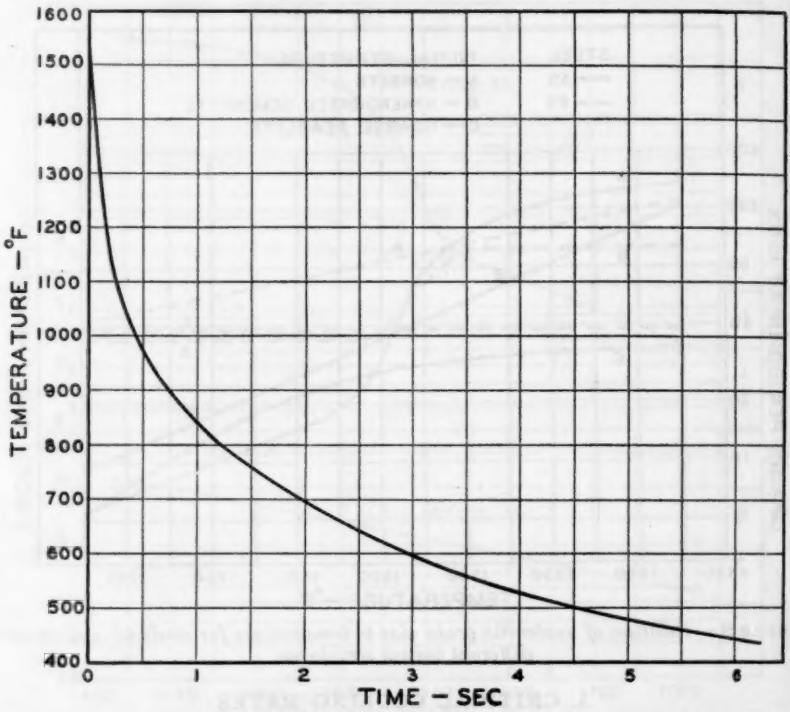

FIGURE 9.—*Time-temperature cooling curve for a ¼-inch square by 0.040-inch thick specimen quenched from 1,550° F.*

Data derived from a photographic record of the string galvanometer.

respectively. The estimated amounts of nodular troostite formed with the various quenching rates are also shown on the charts and the curves represent the relation of the critical cooling time to the quenching temperature values.

For the purpose of convenient comparison, the critical cooling rate versus quenching temperature curves for all three initial structural conditions of each steel are summarized in figure 16.

When quenched from 1,425° F, the critical cooling rates for the two steels were approximately the same whether the initial structures were sorbitic or spheroidized, that is, the steels hardened with equal

[13] H. J. French and O. Z. Klopsch, Trans. Am. Soc. Steel Treating **6**, 251–294 (1924).

facility. The critical cooling rates for the two steels were also the same when the initial structure was coarse pearlite, but this rate was

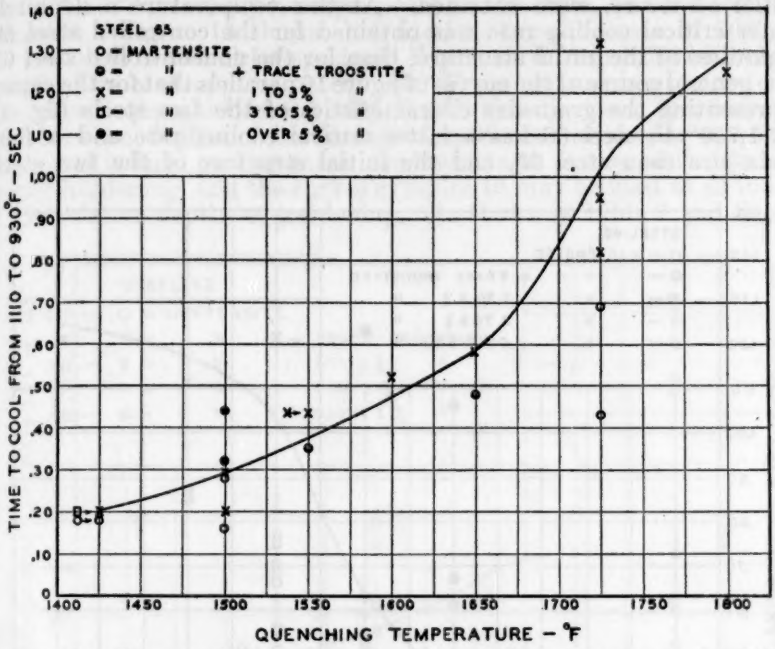

FIGURE 10.—*Time required for steel 65, with an initial structure of spheroidized cementite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

much lower than that of the initially sorbitic or spheroidized steels. With quenching temperatures in the lower range—1,425 to about

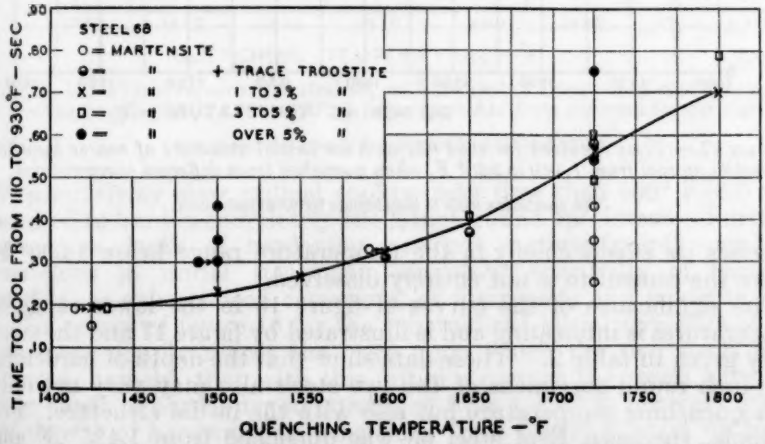

FIGURE 11.—*Time required for steel 68, with an initial structure of spheroidized cementite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

1,600° F—the critical cooling rate for either steel is clearly influenced by the initial structure. Above 1,600° F the curves separate into two

groups (one for each steel). At 1,725 to 1,750° F, critical cooling rates, which appear to be characteristic of the steels irrespective of their initial structure, were obtained. At this temperature a definitely faster critical cooling rate was obtained for the controlled steel 68, regardless of the initial structure, than for the noncontrolled steel 65. The general course of the curves of figure 16 parallels that for the curves representing the grain-size characteristics of the two steels (fig. 8). At 1,750° F, steel 68 has a faster critical cooling rate and a finer grain size than steel 65, and the initial structure of the two steels

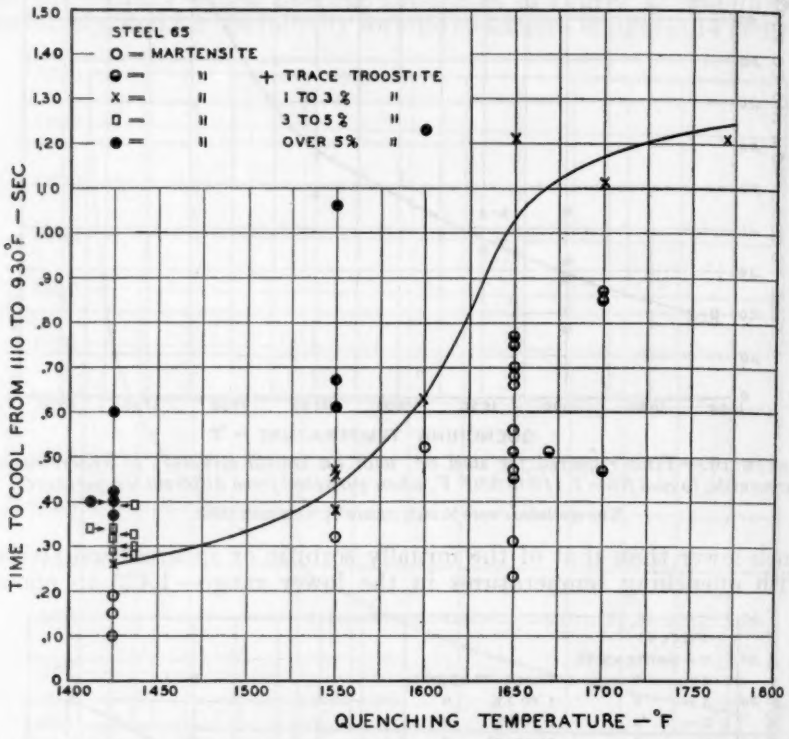

FIGURE 12.—*Time required for steel 65, with an initial structure of coarse lamellar pearlite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

exercises its effects chiefly in the temperature range below 1,600° F, where the cementite is not entirely dissolved.

The significance of the curves of figure 16 in the lower range of temperatures is interesting and is illustrated by figure 17 and the summary given in table 2. These data show that the depth of hardening of ¾-inch round specimens of the two steels also may vary not only with quenching temperature but also with the initial structure. For example, specimen E of steel 65 was quenched from 1,425° F and specimen F of the same steel was quenched from 1,500° F. A higher quenching temperature normally results in deeper hardening, especially in a noncontrolled steel such as steel 65. It is obvious from figure 17,

however, that specimen F has hardened less deeply than specimen E. This difference is due to the different initial structure of the specimens, E having initially a coarse pearlitic structure, and F a sorbitic structure. Figure 16 shows that a critical cooling rate of 900° F per second is obtained for specimen F quenched from 1,500° F, while a critical rate of approximately 700° F per second is obtained for specimen E quenched from 1,425° F. Obviously, there is a correlation between depths of hardening of specimens of similar size and shape and critical cooling rates, the lower rates corresponding to the deeper-hardening, and the curves of figure 16 may be used as an index of the relative depths of hardening. As shown in table 2 and figure

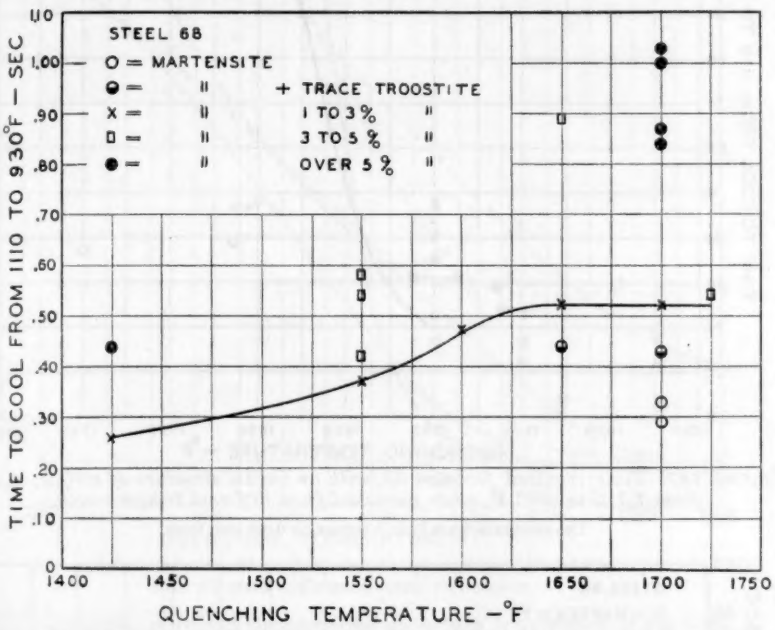

FIGURE 13.—*Time required for steel 68, with an initial structure of coarse lamellar pearlite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

17, a relatively slow critical cooling rate (less than 500° F/sec) was required to harden completely the ¾-inch round specimens. Furthermore, the depth of hardening was not materially influenced by variations in initial structures consisting essentially of lamellar pearlite, or spheroidized cementite, or martensite and troostite.

The curves of figure 16 for the spheroidized initial structure of the two steels simply reflect the basis upon which the two steels were selected, namely, that with this initial structure the steels have the same depth of hardening on quenching from 1,425° F, but very different depths of hardening on quenching from 1,550° F, steel 65 being the deeper-hardening steel. With this in mind, the significance of initial structure is well illustrated by the fact that steel 68 with an

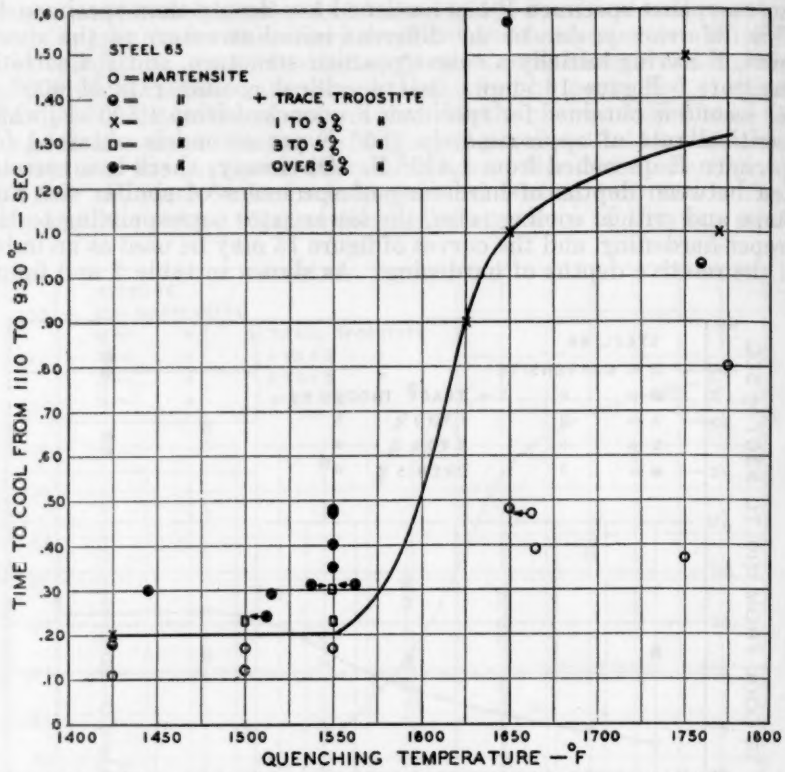

FIGURE 14.—*Time required for steel 65, with an initial structure of sorbite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

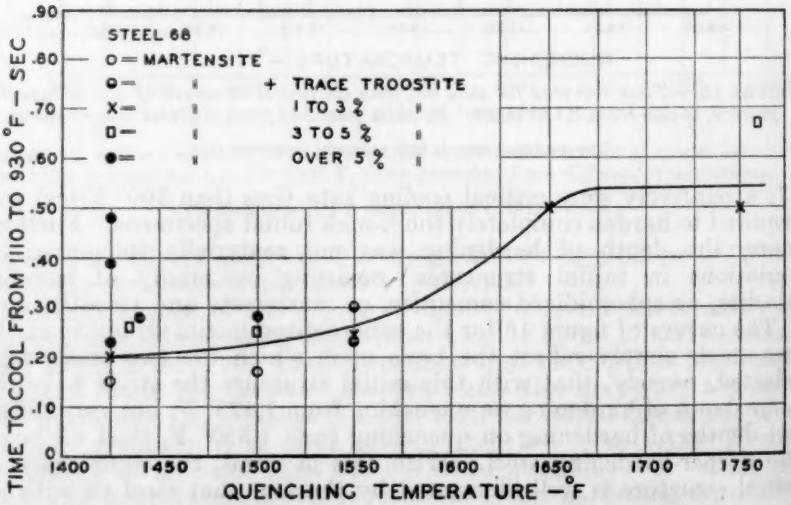

FIGURE 15.—*Time required for steel 68, with an initial structure of sorbite, to cool from 1,110 to 930° F, when quenched from different temperatures.*

The specimens were ¼ inch square by 0.040 inch thick.

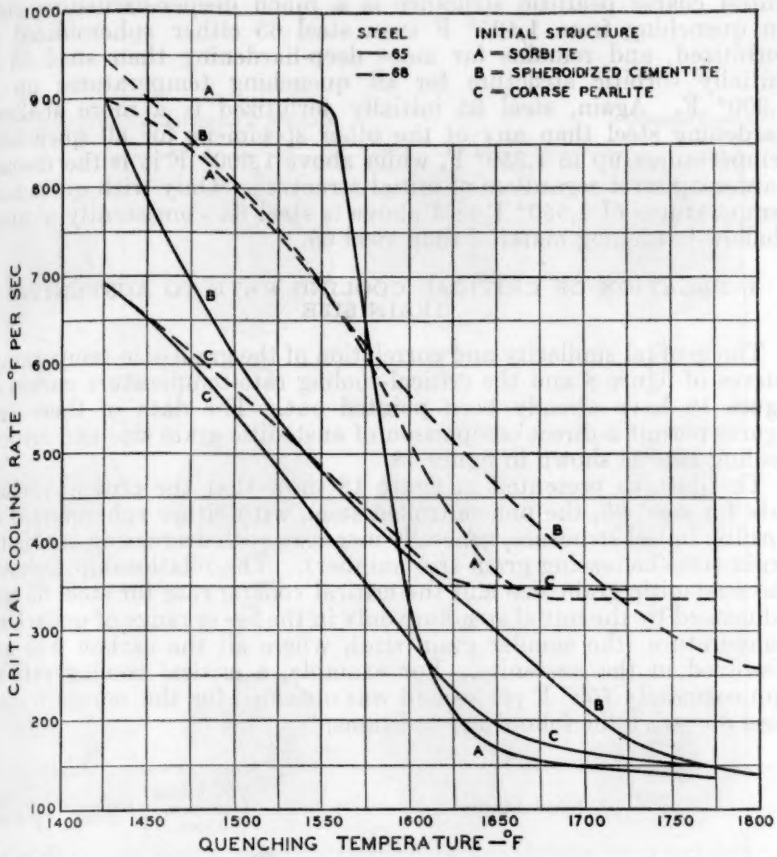

FIGURE 16.—*Relation of critical cooling rate to quenching temperature for steels 65 and 68 with different initial structures.*

TABLE 2.—*Relations of initial structure and quenching temperature to the depth of hardening of ¾-inch rounds of steels 65 and 68*

Steel	Initial structure before hardening	Quenching temperature [1]	Critical cooling rate [2]	Relative depth of hardening of ¾-inch rounds	
				Penetration	Etched section shown in fig. 17
		°F	°F/sec		
65	Spheroidized cementite	1,425	900	Shallow	A
65	do	1,550	480	Deep	B
65	Lamellar pearlite	1,425	[3]	Shallow	C
65	do	1,550	[3]	Deep	D
65	Coarse lamellar pearlite	1,425	700	Intermediate	E
65	Sorbite	1,500	900	Shallow	F
65	Martensite and troostite	1,550	[3]	Deep	G
68	do	1,550	[3]	Shallow	H
68	Spheroidized cementite	1,425	950	do	I
68	do	1,550	700	Intermediate	J
68	Lamellar pearlite	1,425	[3]	Shallow	K
68	do	1,550	[3]	Intermediate	L
68	Coarse lamellar pearlite	1,425	700	Shallow	M
68	do	1,550	480	Deep	N
68	Sorbite	1,425	900	Shallow	O
68	do	1,550	700	Intermediate	P

[1] Heated for 35 minutes, quenched in brine. [2] Data from fig. 16. [3] Not determined.

initial coarse pearlitic structure is a much deeper-hardening steel on quenching from 1,425° F than steel 65 either spheroidized or sorbitized, and remains far more deep-hardening than steel 65 of initially sorbitic structure for all quenching temperatures up to 1,600° F. Again, steel 65 initially sorbitized is a more shallow-hardening steel than any of the other specimens for all quenching temperatures up to 1,550° F, while above 1,600° F it is the deeper-hardening steel regardless of initial structure. Only with quenching temperatures of 1,650° F and above is steel 68 consistently a more shallow-hardening material than steel 65.

4. RELATION OF CRITICAL COOLING RATE TO AUSTENITIC GRAIN SIZE

The general similarity and correlation of the grain-size-temperature curves of figure 8 and the critical-cooling rate-temperature curves of figure 16 have already been pointed out. The data of these two figures permit a direct comparison of austenitic grain size and critical cooling rate as shown in figure 18.

The data as presented in figure 18 show that the critical cooling rate for steel 65, the noncontrolled steel, with either spheroidized or sorbitic initial structure, generally increases with decreasing austenitic grain size (increasing grain-size number). The relationship between the austenitic grain size and the critical cooling rate for steel 65 was influenced by the initial structure only in the lower range of quenching temperature (the smaller grain size), where all the carbon was not dissolved in the austenite. For example, a critical cooling rate of approximately 700° F per second was obtained for the noncontrolled steel 65 under the following conditions:

Initial structure	Quenching temperature	Austenite grains	ASTM grain no.
	°F	Per sq in. at×100	
(A) Fine lamellar pearlite or sorbite	1,570	100	8
(B) Spheroidized cementite	1,475	130	8
(C) Coarse lamellar pearlite	1,425	40	6

Thus, the critical cooling rates were identical (700° F/sec) for average austenitic grain sizes from 130 to 40 grains per square inch at 100-diameters magnification (grain-size number 8 to 6). This circumstance is probably attributable to differences in the amount and distribution of carbon in the austenite. Considering the recognized effect of grain size alone, a lower critical cooling rate might be anticipated for the specimen containing 40 austenitic grains per square inch at 100-diameters magnification than for specimens of the same steel having 100 or 130 grains per square inch at 100-diameters magnification. When the specimen of initially coarse pearlitic structure is heated to 1,425° F it is a relatively short distance above the eutectoid temperature; a limited proportion of the cementite goes into solution; a considerable number of free cementite particles remain within the austenite grains and a network of cementite outlines the grains (fig. 19, C). Both the relatively low carbon content of the austenite and

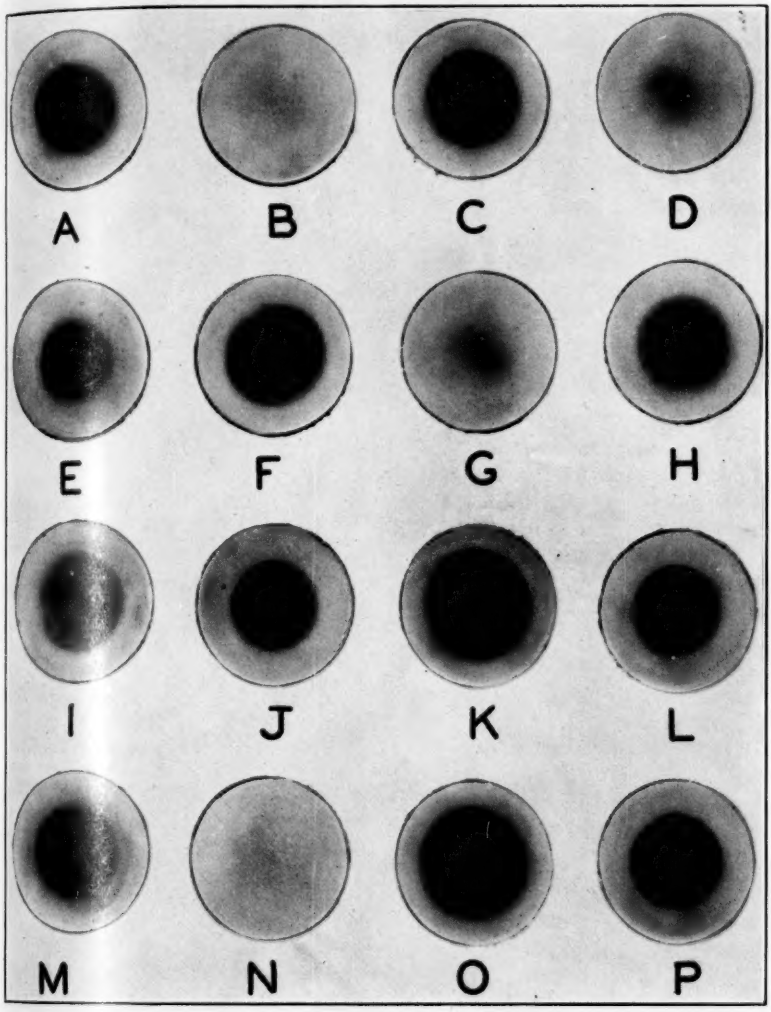

FIGURE 17.—*Relative depth of hardening of three-quarter-inch rounds of steels 65 and 68, with different initial structures, quenched from different temperatures.*

Refer to table 2 for the initial structures (before hardening) and quenching temperatures used. The prepared cross sections were etched in 1 percent nitric acid in alcohol to darken the unhardened portions.

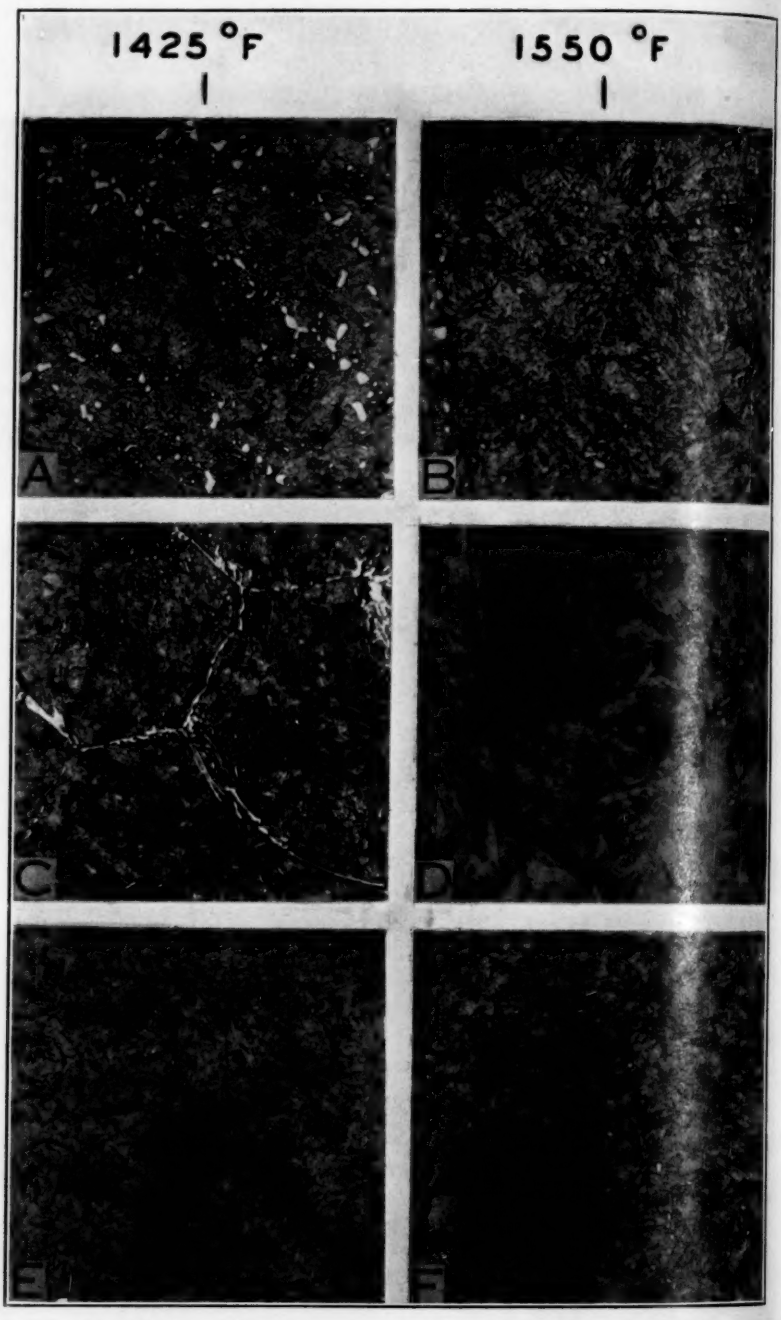

FIGURE 19.—*Effects produced by the initial structure on the free carbides remaining in specimens of steel 65 quenched from 1,425° or 1,550°F.*

A and *B*, Initial structure of spheroidized cementite; *C* and *D*, initial structure of coarse lamellar pearlite *E* and *F*, initial structure of sorbite. Etched with 1 per cent nitric acid in alcohol, × 500.

the presence of a considerable number of free cementite particles within the grain, which supply nuclei for austenite decomposition in the Ar′ temperature range, act to increase the critical cooling rate and oppose the effect of the relatively large grain, which decreases the critical cooling rate. The resultant rate thus becomes the same as

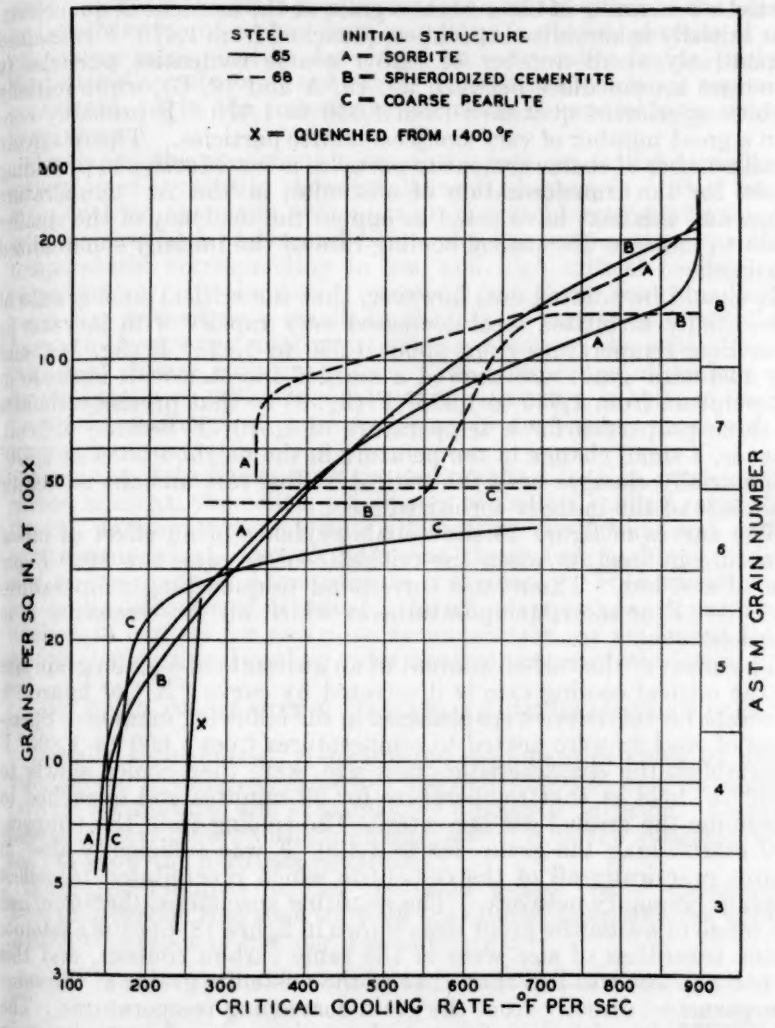

FIGURE 18.—*Relation of austenitic grain size to critical cooling rate for steels 65 and 68 with different initial structures.*

that of the much finer-grained specimen heated from an initial sorbitic structure to 1,570° F, where the carbon content of the austenite is higher than in the coarse pearlitic specimen just described and where less free cementite remains (fig. 19, F).

The initially spheroidized specimen of steel 65 has a grain size at 1,475° F slightly smaller than the initially sorbitic specimen at

1,570° F, and would be expected to give a relatively higher critical cooling rate. This specimen also should have an austenite of somewhat lower carbon content, tending to increase further the critical cooling rate. Yet actually the observed rate was again 700° F per second. The factor which probably offsets any such tendency to increase the critical rate is a difference in the number of free cementite particles remaining in the austenite grain at the moment of quenching. The initially spheroidized specimen quenched from 1,475° F contained a relatively small number of rather coarse cementite particles (a structure intermediate between fig. 19, A and 19, B), while initially sorbitic specimens quenched from 1,550 to 1,570 ° F probably contain a great number of very small cementite particles. The relatively small number of coarse cementite particles is less effective in providing nuclei for the transformation of austenite, in the Ar′ temperature range and this may have acted to oppose the tendency of the smaller grain to increase the critical cooling rate of the initially spheroidized specimen.

It should be pointed out, however, that the critical cooling rate of the initially sorbitized steel decreased very rapidly with increase in quenching temperature from about 1,550 to 1,625° F (fig. 16), and the austenitic grain size showed a marked increase with increase in temperature from 1,550 to 1,625° F (fig. 8) so that precise estimates of these properties for a temperature of 1,570° F became difficult. That is, a small change in temperature in the neighborhood of 1,570° F materially changes both the critical cooling rate and the austenitic grain size of the initially sorbitized steel.

The curves of figure 18 show little evidence of an effect of initial structure in steel 65 when the critical cooling rates are 300° F per second and less. These rates correspond to quenching temperatures of 1,600° F or more, temperatures at which all the cementite is in solution.

The effect of the carbon content of an austenite of a given grain size on the critical cooling rate is illustrated by curve "X" of figure 18. The data for this curve were obtained in the following manner: Specimens of steel 65 were heated to temperatures from 1,600 to 1,800° F to establish the characteristic grain size, were then cooled slowly to 1,400° F, held at that temperature for 30 minutes and quenched to determine the critical cooling rates. The cooling from the temperature establishing the grain size to 1,400° F was sufficiently slow to permit practically all of the cementite which precipitated to collect as grain boundary network. The resulting specimens, therefore, had the range of austenitic grain sizes shown in figure 18, but the austenite grains regardless of size were of the same carbon content, and this carbon content was less than that of the austenite grains of the same size quenched directly from the grain coarsening temperatures. The increase of the critical cooling rate for a given size of austenite grain caused by a lower carbon content of the austenite is very marked.

As has already been shown in figures 8 and 16, both austenitic grain sizes and critical cooling rates for temperatures between 1,425 and 1,775° F cover appreciably narrower ranges for the controlled steel 68 than for the noncontrolled steel 65. Steel 68 with an initial structure of coarse pearlite covers a range of critical cooling rates from 700 to 350° F/sec with no change in austenitic grain size. This holds

true not only for the range of quenching temperatures below the A_{cm} temperature, where differences in the amount and uniformity of distribution of carbon dissolved in the austenite may effect changes in critical cooling rates, but also is true for quenching temperatures considerably above the A_{cm} temperature, where such effects of carbon from cementite should be absent. In this higher range of quenching temperature, if the grain size is constant and the effect of the amount and distribution of carbon from cementite is absent, changes in critical cooling rates must be dependent on some other factor, probably the nucleation effects of the oxides or carbides which are commonly considered to be the influencing elements in controlling austenitic grain sizes.

Similarly, the specimens of steel 68 with an initial structure of spheroidized cementite show pronounced changes in critical cooling rates with no change in austenitic grain size for ranges of quenching temperatures both above and below the A_{cm} temperature (quenching temperatures corresponding to low and high critical cooling rates, respectively). In the lower range of quenching temperatures the grain size is uniformly small; in the higher range, uniformly large. Between these two temperature ranges, however, the critical cooling rate does change with grain size. The wide range of cooling rates for the specimens with an initial sorbitic structure, in spite of the relatively slight change in grain size, may be tentatively explained in a similar manner.

Since the grain size is constant and no effect is to be expected from carbon content, the continued change of critical cooling rates above the A_{cm} temperature may be an indication that oxide and carbide constituents which control grain size themselves undergo modification as the quenching temperature is increased. Such modifications are in the direction of decreasing the effectiveness of such particles as nucleation centers for austenite decomposition, as evidenced by the fact that the critical cooling rates become progressively lower.

5. RATE OF HEATING TO HARDENING TEMPERATURES

Initially spheroidized, ¾-inch round specimens of steels 65 and 68 were heated at different rates to 1,425 and 1,550° F, held at temperature for 35 minutes, and subsequently quenched in brine. Depth of hardening was determined by etching a section of the quenched specimen to show the hardness penetration.

The time required for the center of ¾-inch round specimens of 1-percent-carbon tool steel to reach the desired temperatures with the different methods of heating was as follows:

Heating medium	Approximate time required for center of ¾-inch round to reach 1,425 or 1,550° F.
	Minutes
Lead bath	1 to 1½
Salt bath	3 to 4
Electric furnace	10 to 13

16372—35——5

The rates of heating used had no significant influence on the depth of hardening of the two steels. Both steels again had similar depths of hardening on quenching from 1,425° F in brine (fig. 1), but quite different hardness penetration on quenching from 1,550° F.

6. RATE OF SPHEROIDIZATION OF CEMENTITE

Specimens of steels 65 and 68, with initial structures consisting essentially of lamellar pearlite, were pack-annealed at 1,300° F for ¼, ¾, 1, 1½, 3, 5, 17, 24, and 48 hours, respectively. Similar specimens were also pack-annealed at 1,340° F for ¾ and 5 hours, respectively. As judged from a microscopical examination of the annealed specimens, there was no marked difference in the rate of spheroidization of the two steels.

7. STRUCTURAL NORMALITY OR ABNORMALITY

Initially spheroidized specimens of steels 65 and 68 were packed in a commercial carburizing mixture and heated with the furnace to 1,725° F, held at that temperature for 8 hours and furnace-cooled. Similar specimens were also packed in sand containing a small amount of charcoal and heated in the furnace together with the above specimens.

Steel 65 had a normal structure after each treatment as evidenced by the continuity of the pearlite grains bounded by a thin layer of cementite, while steel 68 was probably more abnormal than normal, as shown by a lack of perfection of the crystallization of the pearlite.

8. PERFORMANCE AS LATHE TOOLS

Lathe tests were made with ¼- by ½-inch tools of steels 65 and 68 which were quenched in brine from different temperatures, namely, 1,425 and 1,550° F, and tempered at 300° F. The lathe tests were made under heavy duty or roughing conditions on a 3½-percent-nickel-steel forging.

TABLE 3.—*Summary of heat treatment of tools and lathe tests made with steels 65 and 68* [a]

Steel	Quenching [b] temperature	Cutting speed	Tool life (minutes)						
			Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Average
	°F	Ft/min							
68	1,425	11	12.6	30.2	14.0	[c] (48)	[c] (48)	35.5	31.4
65	1,425	11	10.8	8.0	8.4	18.5	[c] (48)	[c] (48)	23.6
68	1,550	11	9.7	[c] (48)	7.7	[c] (48)	6.0	5.8	20.9
65	1,550	11	[c] (48)	27.2	7.1	5.1	[c] (48)	14.0	24.9
68	1,425	12	6.3	11.2	32.1	26.6	14.4	1.8	15.5
65	1,425	12	5.9	5.2	10.3	4.7	3.7	5.0	5.8
68	1,550	12	5.4	13.6	5.7	6.6	10.0	5.2	7.8
65	1,550	12	4.6	3.8	.8	6.8	23.2	3.3	7.1

[a] The lathe tests were made "dry" with a feed of 0.028 inch/rev and 3/16-inch depth of cut on annealed 3½-percent nickel (SAE 2340) steel with a tensile strength of approximately 88,000 lb/in². The tools were ¼ by ½ inch, with 6° front and side clearance, 8° back slope, 14° side slope and ⅛-inch nose radius.

[b] Initially annealed to produce spheroidized cementite. Quenched in brine; tempered 1 hour at 300° F, air-cooled.

[c] Test stopped after 48 minutes, tool did not fail.

The heat treatments of tools and details of the lathe tests are summarized in table 3. The results show that the tools of steel 68 ("shallow-hardening") quenched from the usual range of hardening

temperature had a somewhat greater average life than those of similarly treated tools of steel 65 ("deep-hardening"). However, the average life of the tools of both steels quenched from 1,550° F was of the same order of magnitude. Furthermore, the variations used in the hardening treatments did not influence the performance of steel 65. No significant differences were, therefore, observed in the lathe tool performance of the two steels initially spheroidized, quenched and tempered, and tested under roughing conditions.

9. CHARPY IMPACT

Charpy impact tests were made on specimens of steels 65 and 68 which were subjected to different heat treatments. All of the specimens were prepared from ¾-inch round bars after a normalizing or annealing treatment and were notched and ground to a standard size before the hardening and tempering treatments.

The heat treatments used, and the Charpy impact values, are summarized in table 4. In the annealed or spheroidized condition (fig. 4, A and B) the impact strength of steel 65 was greater than that of steel 68, but in the normalized or lamellar pearlitic condition the strength of steel 68 was greater than that of steel 65. However, these differences were small as were the differences observed in the strengths of the two steels after similar hardening and tempering treatments.

TABLE 4.—*Summary of Charpy impact tests made on steels 65 and 68*

Steel	Heat treatment				Charpy impact
	Annealing temp [1]	Normalizing temp [2]	Quenching temp [3]	Tempering temp [4]	
	°F	°F	°F	°F	Ft-lb
65	1,425	None	None	None	4.5
68	1,425	do	do	do	3.0
65	None	1,575	do	do	2.3
68	Mill annealed [5]	1,575	do	do	3.0
65	1,425	None	1,425	do	0.6
65	1,425	do	1,425	350	0.9
65	1,425	do	1,425	680	2.6
65	1,425	do	1,550	None	0.5
65	1,425	do	1,550	350	0.5
65	1,425	do	1,550	680	0.5
68	Mill annealed [5]	do	1,425	None	0.7
68	do	do	1,425	350	1.2
68	do	do	1,425	680	3.6
68	do	do	1,550	None	0.6
68	do	do	1,550	350	0.7
68	do	do	1,550	680	1.5

[1] At temperature 2 hours.
[2] At temperature 1 hour.
[3] Heated in salt bath at temperatures as indicated for 20 minutes, quenched in brine.
[4] Heated in oil or nitrate bath at the temperatures as indicated for 1¼ hours, air-cooled.
[5] Spheroidized structure.

10. ROCKWELL HARDNESS AND SUSCEPTIBILITY TO GRINDING CRACKS

Initially spheroidized specimens approximately ½ inch square by 3 inches long of steels 65 and 68 were quenched from 1,425° F in brine and a similar series in water. The quenched specimens were used for

the determination of Rockwell hardness and for grinding and etching tests.

The Rockwell hardness, grinding, and etching tests are summarized in table 5. When quenched from 1,425° F. in brine both steels had the same average surface hardness; namely, Rockwell C 67.5, and no soft spots were observed on the surfaces of the specimens. When quenched in water, the average value of the surface hardness of steel 65 was about a point higher than of steel 68 (Rockwell C 66.5 and 65.5, respectively) and the latter steel also had the higher index for soft spots. The steels as treated showed no difference in susceptibility to hardening or grinding cracks.

TABLE 5.—*Summary of Rockwell hardness, grinding, and etching tests made on steels 65 and 68*

Steel	Quenched [1] from 1,425°F into—	Rockwell hardness C [2]		Index for soft spots [5]	Grinding cracks [6]	Appearance after etching [7]
		Average [3]	Normal [4]			
65	Water	66.5	67.0	2	None	Slightly mottled area on 2 surfaces.
65	Brine	67.5	67.5	0	do	Clear.
68	Water	65.5	66.5	7	do	Small mottled area on 4 surfaces.
68	Brine	67.5	67.5	0	do	Clear.

[1] Specimens were first annealed, then machined and ground to approximately .515 by .520 by 3.0 inches. Heated in salt bath for 35 minutes for hardening.
[2] Rockwell hardness determinations were made on the four 0.5 -by 3-inch surfaces of each specimen after hardening and without grinding. Ten readings regularly spaced, were made on each of these surfaces.
[3] Average of all 40 readings.
[4] Average of readings of 60 or more.
[5] Rockwell readings below 60 were taken as an indication of softness and were given the following weights: 60 to 55=1; 55 to 50=2; 50 to 45=3; below 45=4.
[6] Ground dry with cuts 0.001 inch deep; 4 cuts made.
[7] Etched, after grinding, in hot aqueous HCl (1:1; 160° F), for 20 minutes.

V. SUMMARY

Two commercial 1-percent-carbon tool steels were selected, on the basis of widely different hardening characteristics, for a detailed study of the relation of the initial structure, prior to heating for hardening, on the austenitic grain size and grain growth. Comparisons of the steels were also made with respect to their behavior in the transformation temperature range during thermal analysis, relative rates of spheroidization of the cementite, Charpy impact strengths, relative susceptibility to grinding cracks, Rockwell hardness values on quenching at different rates, structural normality, performance as lathe tools, and the effect of rate of heating to the hardening temperatures on the depth of hardening.

Measurements of austenitic grain size were made and critical cooling rates were determined for the temperature range from 1,425 to 1,775° F. The data thus secured permitted the derivation of grain size critical cooling rate relations throughout this range of temperature.

For quenching temperatures below that at which all the carbon is completely dissolved in the austenite, both the austenitic grain size and critical cooling rates are influenced to a large degree by the initial structure of the steels. Above this temperature, each steel approached both a grain size and a critical cooling rate which was characteristic of the steel regardless of its initial structure. At the highest temperature, namely, 1,775° F, the characteristic grain

size was smaller and the characteristic critical cooling rate was higher for the steel known to have been made under conditions producing so-called "controlled steel." The effect of grain size on the critical cooling rates was marked in the "noncontrolled" steel throughout the entire range of quenching temperatures. The influence of the initial structure was also evident at the lower quenching temperatures. The critical cooling rate of the controlled steel, however, may change very appreciably with little or no change in austenitic grain size. At the lower quenching temperatures, differences in carbon content and carbon distribution in the austenite may be the controlling factor, but at higher temperatures oxides or carbides introduced for grain control are probably the effective factors in changing the critical cooling rate.

The initial structure of the controlled steel exerts an influence on the grain size-critical cooling rate relations at both low and high quenching temperatures.

A few determinations made on a noncontrolled steel indicated that the critical cooling rate of this steel with austenitic grains containing carbon above eutectoid composition is lower than that for the same steel with grains of the same size containing about eutectoid proportions of carbon.

The differences observed in the transformation of the two steels on slowly heating to the temperature range of austenite are believed to be caused by a variation in the rates of carbon diffusion, the controlled steel having a higher rate than the noncontrolled steel.

The controlled steel was more abnormal in structure than the noncontrolled steel on slowly cooling from the austenite temperature range.

Variations in rates of heating to the hardening temperatures did not influence the depth of hardening of the two steels.

No marked differences were observed in the behavior of the two steels with respect to their tool performance in la the cutting, Charpy impact values, and Rockwell hardness values, and susceptibility to grinding cracks.

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ATOMIC WEIGHT OF GALLIUM

By G. E. F. Lundell and James I. Hoffman

ABSTRACT

In this determination of the atomic weight of gallium, weighed portions of the pure metal were converted to the hydroxide, the sulphate, and the nitrate, respectively. These were then heated until they were changed to the oxide, Ga_2O_3, which was finally ignited at 1,200 to 1,300° C. By this procedure, the atomic weight is related directly to that of oxygen.

Preliminary tests showed that the metal was free from an appreciable film of oxide and did not contain occluded gases. The highly ignited oxide, obtained through the hydroxide or the sulphate, contained no gases and was not appreciably hygroscopic. The oxide obtained by igniting the nitrate was less satisfactory. To make possible the correction of the weights to the vacuum standard, the density of the oxide was also determined, and found to be 5.9_5 g/cm³.

The value for the atomic weight based on this work is 69.74.

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I. INTRODUCTION

The atomic weight of gallium was determined by Lecoq de Boisbaudran soon after he discovered the element,[1] and later by T. W. Richards and W. M. Craig.[2] Boisbaudran's determinations were made by converting gallium ammonium alum to gallic oxide and by converting the metal to the oxide through the nitrate. He obtained 70.12 and 69.70, respectively, as values for the atomic weight by these two methods. Richards and Craig prepared pure gallium trichloride ($GaCl_3$)

[1] Compt. rend. 86, 941 (1878) and J. Chem. Soc. (Abstracts) 34, 646 (1878).
[2] J. Am. Chem. Soc. 45, 1155 (1923).

and determined the quantity of chlorine in combination with the gallium by precipitating and weighing the chlorine as silver chloride, thus relating the atomic weight of gallium to that of silver (107.88) through chlorine (35.458). Their result, 69.716, becomes 69.720, if the present value for the atomic weight [3] of chlorine, 35.457, is used in the calculation. The scarcity of gallium and the difficulty of obtaining it in the pure state probably account for the fact that so few determinations of its atomic weight have been made.

Recently metallic gallium, at least 99.999 percent pure, was prepared by one of the authors,[4] and it was deemed advisable to determine the atomic weight, with this very pure metal as the starting point. The most obvious and attractive method seemed to be that of converting the metal to the oxide through the hydroxide, the sulphate, and the nitrate, respectively, thus directly relating the atomic weight to that of oxygen and avoiding errors that might exist in determinations by less direct methods.

II. PRELIMINARY TESTS

At the outset, it was necessary to make sure that both the metal and the oxide, Ga_2O_3, are suitable for this type of work. T. W. Richards and E. F. Rogers [5] found that many oxides, especially those obtained by igniting the nitrate, contained gases which they did not succeed in driving out by heating in a vacuum or by heating with a blast lamp. These authors determined the gases by dissolving the oxides in acids and then measuring the volume of the gases liberated. Obviously their work was confined to oxides, such as those of magnesium, zinc, and nickel, which are soluble in acids.

In the present work it was found that gallic oxide, ignited at 1,100 to 1,300° C, is insoluble in acids, but that it can be dissolved in hot diluted hydrochloric acid (2+3) [6] if the oxide has not been heated above 850° C. In the method employed by us for the determination of the atomic weight, the oxide was heated at 1,200 to 1,300° C until constant weight was attained, but it seemed reasonable to assume that if it could be shown that the oxide ignited at 850° C contained no gases, then an oxide prepared in a similar way and finally ignited at 1,200 to 1,300° C would be very unlikely to contain any.

Three 0.5-g portions of gallic oxide were therefore prepared by igniting the hydroxide, the sulphate, and the nitrate, respectively, for 5 hours at 800 to 850° C. These were then dissolved in 20 ml of diluted hydrochloric acid (2+3) in a glass tube of such shape that any liberated gases would be trapped in a small graduated portion of the tube.[7] Before use, the diluted hydrochloric acid was heated on the steam bath in a manner similar to that employed in dissolving the gallic oxide, to make certain that dissolved gases that could be liberated by such heating would be expelled. A bubble of gas, the volume of which was estimated to be about 0.1 ml, was obtained from the oxide derived from the nitrate. The others did not yield a trace of gas.

[3] J. Am. Chem. Soc. 57, 787 (1935)
[4] James I. Hoffman, J. Research NBS 13, 665 (1934) RP734.
[5] Proc. Am. Acad. Arts, Sci. 28, 200 (1893).
[6] This denotes two volumes of concentrated hydrochloric acid (specific gravity 1.18) diluted with three volumes of water. This system of specifying diluted acids is used throughout this paper. If no dilution is specified, the concentrated reagent is meant.
[7] The method of determination was essentially that used by Richards and Rogers. Proc. Am. Acad. Arts Sci., 28, 200 (1893).

The foregoing determinations strongly indicated that gallic oxide, derived from the hydroxide or the sulphate by igniting to constant weight at temperatures above 850° C, would not contain any gases, but a direct determination on a portion of oxide, ignited at 1,300° C, was deemed highly desirable. A 0.5-g portion was accordingly placed in a platinum tubulated crucible containing 6 g of borax that had previously been fused to free it from gases. The crucible was then sealed to a manometer and evacuated. The volume of the evacuated system was about 40 cc. The borax and gallic oxide were fused at the lowest temperature possible. During the heating required for the fusion the mercury in the manometer remained practically stationary, and when the tube had cooled to the original temperature, the mercury stood at its original level. This indicated the absence of any gases in the gallic oxide, but a similar determination on a 0.5-g portion of zinc oxide, prepared by igniting the nitrate and known to contain 0.30 ml of gas,[8] yielded only about 0.1 ml of gas. Subsequent tests showed that the viscous molten borax in the quantity used can hold 0.3 ml of gas in an evacuated system, at the temperature that was permissible, even though no large bubbles are visible.

The foregoing procedure was then modified so that it included fusion in borax and measurement of the gas after solution of the cooled melt in acid. The fusion was made in the tubulated platinum crucible as described, the platinum top of the crucible was removed after cooling, and a glass top, fitted with a graduated tube, was sealed in its place. Diluted hydrochloric acid (2+5) was then added, and the liberated gases were measured. Aside from the fact that solution of the melt was very slow, this latter part of the procedure was essentially the same as that used in determining the gases in the oxide directly by solution in acid. The borax in all the determinations and blanks was heated in a vacuum for 3 hours before use. Three blank determinations on 6-g portions of borax ($Na_2B_4O_7.10H_2O$) yielded 0.10, 0.15, and 0.10 ml of gas, respectively. Two determinations on 0.5 g of Ga_2O_3, derived from the hydroxide and sulphate, yielded 0.15 and 0.15 ml of gas, respectively. A single determination on a sample of zinc oxide, known to contain 0.30 ml of gas, yielded 0.25 ml after subtracting 0.10 ml as a blank for the borax. This method is not to be recommended for accurate work on the determination of gases in insoluble oxides because the blanks are too high and inconsistent, but for the present purpose the results show that either no gas or a negligible quantity is contained in gallic oxide obtained by igniting the hydroxide or the sulphate, and finally heating to 1,300° C.

Of all the oxides investigated by Richards and Rogers, that of magnesium, prepared by igniting the nitrate, contained the most gas. For example, one 0.5-g portion which had been heated over the blast lamp for 1¼ hours contained 5.86 ml of gas (mostly nitrogen and oxygen). If it could be shown that prolonged ignition at 1,300° C would expel all gases from this oxide, it was deemed probable but not necessarily certain that similar ignitions would free gallic oxide from gases, provided any were present. A 5-g portion of magnesium oxide was prepared by igniting the nitrate and finally heating for 2 hours at 1,100° C. By dissolving in acid and measuring the volume

[8] The amount was determined by dissolving in acid and measuring the volume as previously indicated.

of the evolved gases, a 1.0-g portion of this oxide yielded 3.1 ml of gas. The remainder of the oxide was then heated for 1½ hours at 1,300° C and the quantity of gas determined in a 1.0-g portion. A volume of 1.7 ml was found. The remaining oxide was then heated at 1,300° C for an additional period of 7 hours. A 1.0-g portion of this yielded only 0.25 ml of gas. As the oxide in all determinations of the atomic weight to be reported in this paper was heated at 1,300° C for at least 15 hours, it is probable that any gases would have been expelled, if they had been present in the oxide at the beginning of the ignition.

To test the gallic oxide for hygroscopicity, a 4-g portion, which had been ignited for 15 hours at 1,300° C, was exposed in an uncovered crucible for 24 hours at relative humidities between 35 and 50 percent. The total gain in weight was only 0.2 mg.

Further tests showed that no change in weight (within the limits of accuracy of weighing) occurred when this strongly ignited oxide was heated for 1 hour at 1,300° C, in an atmosphere of oxygen or nitrogen. This, in addition to the fact that in the ignition of one 4-g portion of oxide no detectable change in weight took place during a period of 46 hours of heating in air at 1,300° C, indicates that the oxide is not appreciably volatile, that it shows no tendency to dissociate at this temperature, and that it contains no lower oxide.

By taking into consideration (1) that gallic oxide, derived from the hydroxide or the sulphate by igniting at 850° C, contains no gas, (2) that either no gas or a negligible quantity was found in the oxide, ignited at 1,300° C, by fusion with borax and solution of the melt in acid, (3) that an oxide like that of magnesium, known to contain gases, tends to lose them on prolonged ignition at 1,300° C, (4) that the highly ignited oxide is not appreciably hygroscopic, and (5) that the oxide shows great stability under varying conditions, it was concluded that this oxide, Ga_2O_3, ignited at 1,300° C, is a suitable compound to use in determining the atomic weight of gallium.

III. PREPARATION AND TESTING OF MATERIALS USED

1. METALLIC GALLIUM

(a) PREPARATION

Two portions of metallic gallium were prepared by the method previously described.[9] Both were at least 99.999 percent pure on the basis of tests given in the reference just cited. One portion of pure metal was that used in determining the melting point [10] and was prepared from crude metal obtained about 15 years ago from Bartlesville, Okla. The other portion was prepared from impure metal recently obtained from the same district.

(b) TESTS FOR OCCLUDED GASES

At no time was there any evidence of the liberation of gases when crystals of the metal were melted under water. Such a test, however, was not regarded as conclusive. A single crystal, weighing 3.5167 g, was placed in a small porcelain boat and weighed, using a similar boat as a counterpoise. The counterpoise and the boat containing the

[9] James I. Hoffman, J. Research NBS **13**, 665 (1934) RP734.
[10] Wm. F. Roeser and James I. Hoffman, J. Research NBS **13**, 673 (1934) RP735.

metal were heated for 30 minutes at 300° C in a stream of hydrogen and then gradually cooled to room temperature in hydrogen. No change in weight was detected. After this the boat containing the gallium was placed in a small Pyrex-glass tube, which was then sealed to a manometer.

After evacuating the system, the gallium in the tube was heated for 30 minutes at 300 to 400° C, after which the system was cooled to room temperature. The mercury stood at the original level, and the gallium in the boat did not show any detectable change in weight. It was therefore concluded that no significant amount of gases was occluded in the crystals. The vapor pressure of gallium is so low (approximately 0.002 mm of Hg at 1,000° C) [11] that loss by volatilization at temperatures below 1,000° C is probably insignificant for any reasonably short period of heating.

(c) TESTS FOR A FILM OF OXIDE ON THE SURFACE OF THE CRYSTALS

The surface of the crystals of metal used in this work was so bright that there seemed small chance that any appreciable film of oxide existed, but the possibility remained that a very thin film might escape simple visual observation. Accordingly, a 4.7-g portion of gallium in the form of small crystals (to give maximum surface for minimum weight of metal) was placed in a hard-glass tube connected to a source of hydrogen and at the outlet to a small tube containing anhydrous magnesium perchlorate, $Mg(ClO_4)_2$. The hydrogen was preheated at about 650° C in a tube containing copper gauze, and the resulting gases were passed through a tube containing ascarite (sodium hydroxide on asbestos) and then through another containing anhydrous magnesium perchlorate, before being admitted into the tube containing the gallium. The metal was heated for 1 hour at 680 to 700° C in a stream of this purified hydrogen, and the increase in weight of the tube containing the anhydrous magnesium perchlorate at the exit end of the hard-glass tube was noted. This increase (0.7 mg) was the same as the average obtained in three blank determinations, which indicated that no appreciable film of oxide was present.

In order to test the efficacy of this procedure, a determination was made in which 2 mg of Ga_2O_3 was substituted for the metallic gallium, immediately after the latter was removed. The absorbing tube in this case showed a net increase in weight of 0.4 mg. A preliminary determination on 9.5 mg of Ga_2O_3 had yielded a net increase in weight in the absorbing tube of 1.8 mg. Strictly quantitative conversion of all the oxygen in the Ga_2O_3 could not be expected because it is not certain whether a lower oxide or the metal is formed by reduction in hydrogen at 680 to 700° C. A. Dupré [12] stated that at a cherry-red heat a lower oxide of gallium is formed, and that at a bright red heat the metal is formed. A. Brukl [13] stated that the lower oxide, Ga_2O, is volatile. In the attempts to reduce the Ga_2O_3 just mentioned, some of the lower oxide must have been formed because a grayish sublimate appeared on the cooler part of the hard glass tube between the heated portion and the exit end. Regardless of the stage of reduction, the

[11] P. Hartech, Z. physik. Chem. **134**, 1 (1928).
[12] Compt. rend. **86**, 720 (1878).
[13] Z. anal. Chem. **86**, 92 (1931).

results indicate that if an appreciable amount of oxide had existed in the metal it would have been detected.

The crystals of metallic gallium were also subjected to two types of optical examination [14] to discover whether there was an oxide coating. A microscopical examination showed that there could be no such coating except as an optically uniform film less than 3 μ (1 μ=.001 mm) thick. To cover the case of films thinner than this, the crystals were examined for the structural colors of thin films.

When an optically reflecting metal surface coated by a transparent film of uniform thickness is illuminated with white light, part of the light is reflected, and part enters the film. This latter is partly reflected and partly absorbed by the metal surface. After multiple reflections, the light which emerges has suffered constructive or destructive interference, depending on the thickness and index of refraction of the film, and on the phase change and angle of the reflection. With normal incidence and negligible phase change at reflection from either surface (as would be expected for a transparent oxide film in optical contact with a metal), a deficiency of blue is observed as a straw color for a film 0.06 μ thick with a refractive index of 1.5. If the film is thicker, the color is brighter and varies according to the sequence of white-center thin-film colors. As the observations are made at increasingly oblique angles, the order of any such color decreases, the change being readily apparent. In the case where a relative phase change of one-half wave length occurs between the two reflections (as would be expected for an oxide film not in optical contact with the metal), a film 0.06 μ thick with a refractive index of 1.5 is gray at normal incidence, but rapidly darkens when viewed at greater obliquities.

The colors of thin films can be produced artificially upon a metal resembling the sample of gallium in polish and reflectivity, by evaporating upon its surface a very pure, very dilute aqueous solution of gelatin or a pure dilute solution of collodion made with anhydrous alcohol and ether. The colors, including the pale straw, corresponding to an optical difference of 0.18 μ (twice the optical thickness of the film), are readily seen and decrease in order as the obliquity of observation increases.

When the face of a gallium crystal was observed under diffused white light, there was no change of its gray color as the crystal was rotated about an axis normal to the direction of observation and lying in the face under observation. This, taken in conjunction with the limits established by the microscopical examination and the fact that gallium is a gray and not a white metal, showed that if a film of oxide with a refractive index as high as 1.5 is present at all, it can not be thicker than 0.06 μ.

Assuming that a cubical crystal, 0.5 cm on an edge, is covered with a film of oxide, 0.06 μ thick, and assuming the density of both the metal and the oxide to be 6, the maximum weight of the oxygen in the film could be only about 0.000014 g and would affect the total weight by only about 1 part in 50,000.

(d) TEST FOR CHLORIDES IN THE CRYSTALS OF METALLIC GALLIUM

Since the metal had been crystallized under dilute hydrochloric acid, a test for chlorides was made by dissolving a crystal, weighing

[14] The optical examinations were made by Charles Proffer Saylor, chemical microscopist at the National Bureau of Standards.

approximately 0.5 g, in diluted sulphuric acid (1+4), neutralizing nearly all the excess acid with ammonium hydroxide, and adding silver nitrate to the faintly acid solution. No turbidity appeared. Under similar conditions, a turbidity appeared in a solution to which 0.02 mg of chloride ion in the form of HCl had been added. It should be noted that pure gallium dissolves very slowly in dilute sulphuric acid.

2. CHEMICAL REAGENTS

Nitric acid, hydrochloric acid, sulphuric acid, and ammonium hydroxide were the only reagents used. The acids, bought on the specifications for analytical reagent chemicals recommended by the Committee on Analytical Reagents of the American Chemical Society, were of such good quality that it was not necessary to purify them. None of them yielded a nonvolatile residue exceeding 0.2 mg when 100-ml portions were evaporated and the residue ignited. As less than 25 ml of the combined acids was involved in any determination, and especially since exactly the same quantities were used in blank determinations, these small amounts of impurities were entirely negligible. The ammonium hydroxide was prepared by passing gaseous ammonia into distilled water contained in a Pyrex flask whose inside surface was covered with paraffin. A 100-ml portion of this ammonium hydroxide yielded a residue weighing less than 0.1 mg, even after the solution had stood in the flask for over 3 months.

3. PLATINUM CRUCIBLES

In work involving prolonged ignitions at high temperatures, it is essential that the crucibles do not change in weight or that two or more crucibles are available that change weight at a uniform rate. The former requirement cannot be met in the case of platinum crucibles.[15] In the determinations of all the results reported in this paper, one platinum crucible, from a series of four having the same composition,[16] was used as a tare. The whole set was heated in a platinum-wound muffle furnace for 5 hours at 1,200 to 1,300° C, cooled and weighed. Then the crucibles were again heated for 15 to 25 hours at 1,200 to 1,300° C, cooled, and weighed. If any crucible, compared with the tare, showed an apparent change in weight of as much as 0.1 mg during this latter period of heating, it was not used. It might be added that in the beginning of the work it was not unusual for at least one crucible out of four to fail to meet these requirements. However, after repeated ignitions, polishings with fine sand, and treatments with hydrochloric acid, all the crucibles remained remarkably constant in weight, as compared with the tare, during successive heatings.

IV. PROCEDURES

1. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE HYDROXIDE

For the conversion of the metal to the oxide, Ga_2O_3, through the hydroxide, one or more crystals were carefully weighed to the nearest

[15] E. Wichers and R. Gilchrist, Serviceability of platinum laboratory ware of various compositions, Publication pending; Abstract in Tech. News Bull. 217, National Bureau of Standards, p. 47 (1935).

[16] Two sets of four crucibles each were used throughout this work. The one was platinum containing about 0.4 percent of iridium, the other was platinum containing about 3.5 percent of rhodium. No difference in performance was noted.

0.05 mg, transferred to a 250-ml Pyrex beaker, and dissolved in a mixture of 40 ml of distilled water, 5 ml of sulphuric acid, 5 ml of nitric acid, and 5 ml of hydrochloric acid. For the determination of a "blank", a dilute solution of aluminum chloride, containing aluminum equivalent to 0.00378 g of Al_2O_3, was transferred to a similar beaker to which the same quantities of reagents had been added. The solution of aluminum chloride was prepared by diluting a more concentrated solution which had been carefully standardized by precipitating the aluminum with ammonium hydroxide and igniting the precipitate to the oxide. From this point the solutions in the two beakers were subjected to the same treatments, and the proper correction for the aluminum added to the "blank" was applied at the end of the determination. The small amount of aluminum chloride was added to the blank to serve as a gatherer of traces of impurities that might otherwise have escaped precipitation.

The solutions in both beakers were evaporated until fumes of sulphuric acid just appeared. They were then cooled, any acid on the inside surface of the beakers was washed down with a jet of water, and the evaporation was repeated to make sure that all chlorides were removed, because chlorides, carried down by the gelatinous precipitate of gallium hydroxide, might result in volatilization of gallium (as $GaCl_3$) during the subsequent ignition.[17] The solutions were again cooled, diluted to 150 ml, a few drops of methyl red indicator added, and then ammonium hydroxide was added until the color of the indicator just turned yellow. The beakers were allowed to stand on the steam bath for 5 minutes. Then the precipitates were transferred to large ashless filters and washed a few times with hot water. The filtrates were slightly acidified with sulphuric acid, evaporated to a volume of 40 to 50 ml, and ammonium hydroxide was again added until the color of methyl red just turned to yellow. After a digestion of 15 minutes on the steam bath, these solutions were allowed to stand over night at room temperature, and any precipitate which separated was removed by filtration and combined with the first precipitate. A dilute solution of ammonium nitrate, whose pH was adjusted to about 6.2, was used for washing this last precipitate.

These filtrates were transferred to clean platinum dishes and heated until nearly all ammonium salts and sulphuric acid were expelled. A few drops of hydrochloric acid and 5 ml of water were added to the residue. The dishes and contents were heated on the steambath for a few minutes, and the solutions were poured through small filters. The filtrates, having volumes of about 10 ml, were neutralized with ammonium hydroxide as before and allowed to stand for 24 hours. As no precipitate appeared in either case, it was concluded that the last of the gallium had been obtained in the preceding precipitation and that all of the aluminum had been precipitated in the case of the blank.

The filters containing the precipitates were transferred to platinum

[17] The fact that almost identical results were obtained for the atomic weight by the three different procedures described in this paper indicates that no loss of gallium occurs when the sulphate is ignited to the oxide or when a solution containing gallium chloride and an excess of sulphuric acid is heated until copious fumes of sulphuric acid are evolved. Further evidence on this point is furnished by the following tests: A solution of gallium sulphate was carefully standardized by precipitating the gallium with cupferron and igniting it to the oxide. One ml of the solution was found to contain 0.003120 g of Ga_2O_3. Two 20-ml portions of this solution (each equivalent to 0.0624 g of Ga_2O_3) were transferred to platinum crucibles and 1 ml of sulphuric acid was added to each. To one was also added 3 ml of hydrochloric acid. The excess of acid was evaporated by heating, first on the steam bath and then indirectly in a radiator. The dry residue was finally ignited to constant weight in the same manner as was done in the standardization. The results obtained, 0.0625 g, and 0.0625 g, respectively, show that no volatilization took place.

crucibles which had been tested for constancy of weight, as previously described. The precipitate containing the aluminum was placed in the crucible used as a tare. After the precipitates were dried in an oven, the crucibles were partially covered and placed in a cold muffle furnace which was gradually heated to about 1,200° C during the course of 6 to 8 hours. The residues were then heated in the tightly covered crucibles at 1,200 to 1,300° C until constant weight was obtained. All final weights remained constant within 0.1 mg during heating for at least 25 hours between 1,200 and 1,300° C, and one of the ignited precipitates was heated for 46 hours between these two temperatures without showing any change in weight. In all weighings the platinum crucible containing the small quantity of aluminum oxide, which was negligibly hygroscopic, was used as a counterpoise. The weight of the residue in the crucible containing the gallic oxide represented the weight of the oxide plus any blank, while the weight of the residue in the crucible used as a tare represented the weight of the aluminum oxide plus the blank. The weights of the blanks, therefore, cancelled each other, and in calculating results, 0.00378 g was subtracted from the weight of the blank because aluminum chloride, equivalent to this weight of aluminum oxide, was added to it in the beginning. Concentrated sulphuric acid was used as the drying agent in the desiccator.

The true weight of gallic oxide was therefore found by subtracting the weight of the crucible used as a tare plus its contents from that of the crucible containing the gallic oxide plus its contents (after making the correction for the aluminum added to the blank). All weighings were made to the nearest 0.05 mg, and all weights were corrected to the vacuum standard. In making these corrections the value, 5.9_1 was used for the density of the solid metal, and 5.9_5 as the density of the oxide, Ga_2O_3. The former is given in the International Critical Tables, vol. 1, p. 104 (1926), but, as no value for the density of the oxide is reported, a determination was made by E. L. Peffer of the volumetric section of the National Bureau of Standards. For this purpose, the pure oxide, obtained in the foregoing procedure, was used. With carbon tetrachloride as the test liquid, a value of 5.97 g/cm^3 was obtained at 27° C. From observations made in kerosene as the test liquid, a value of 5.93 g/cm^3 was found. The value used, 5.9_5, is the average of the results obtained by the two procedures.

The results obtained by converting the metal to the oxide through the hydroxide are shown in table 1.

TABLE 1.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the hydroxide*

[In making the weighings, only 0's and 5's were recorded in the fifth decimal place. Figures other than these are a result of the correction of the recorded values to the vacuum standard, and hence are still subject to the same uncertainty as the recorded values.]

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1[a]	0.86526	1.16307	69.73_0
2[a]	1.25888	1.69205	69.75_0
3[b]	1.23368	1.65815	69.75_3
4[b]	3.45532	4.64464	69.72_7
5[b]	2.97452	3.99838	69.72_8
			69.73_7 = Average.

[a] = first lot of metal. [b] = second lot of metal.

2. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE SULPHATE

The metal was weighed, dissolved, and the nitric and hydrochloric acids removed by evaporation as in the previous procedure. Pyrex beakers of 100-ml capacity were used, and exactly the same quantities of acid were carried along as a blank in a similar beaker. The gallium sulphate and excess sulphuric acid were transferred to a platinum crucible that had been tested for constancy of weight as compared with a similar crucible as a tare in the manner previously described. The contents of the beaker containing the blank were transferred to the crucible used as a tare. The small beakers were repeatedly rinsed with water and the rinsings added to the contents of the crucibles. These additions were made possible by evaporating part of the water from the crucibles between rinsings.

When it was certain that all the gallium sulphate had been transferred, as much as possible of the water was evaporated on the steam-bath. Then the crucibles were partially covered and transferred to radiators, and heat was very gradually applied until the excess sulphuric acid was volatilized. The crucibles and contents were next placed in a muffle furnace which was gradually heated until sulphur trioxide began to be evolved. This occurred at about 700° C, and during this evolution, the temperature was regulated to remain practically constant in order to avoid too rapid a decomposition of the sulphate, which might result in mechanical losses. After sulphur trioxide ceased to be evolved, the crucibles were tightly covered, and the temperature was raised to 1,200 to 1,300° C. The ignition was then continued until constant weight was obtained. A somewhat longer period of ignition was required than in the case of the hydroxide, but no particular difficulty in arriving at constant weight was experienced. The results obtained by this procedure are shown in table 2. All weights are reduced to the vacuum standard.

TABLE 2.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the sulphate*

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1[a]	1.15767	1.55604	69.74_5
2[a]	1.53230	2.05967	69.73_3
3[b]	2.48716	3.34320	69.73_9
4[a]	3.09080	4.15443	69.74_1
			69.73_7=Average.

[a]=first lot of metal.
[b]=second lot of metal.

3. CONVERSION OF METALLIC GALLIUM TO GALLIC OXIDE THROUGH THE NITRATE

The metal was weighed to the nearest 0.05 mg, transferred to a 100-ml Pyrex beaker, and dissolved in a mixture of 40 ml of distilled water, 5 ml of hydrochloric acid, and 5 ml of nitric acid. Exactly the same quantities of acid were carried along as a blank in a similar beaker. When solution was complete, the water and excess of acids were evaporated on the steam bath. Ten ml of diluted nitric acid

(1+1) was added to both the blank and the beaker containing the gallium, and the solutions were evaporated as far as possible on the steam bath. This addition of nitric acid and the evaporation were repeated 5 times to make as certain as possible that all chlorides were expelled. After the last evaporation, the residue in the beaker containing the gallium was dissolved in 10 ml of diluted nitric acid (1+1) and transferred to a platinum crucible which had been carefully weighed and tested for constancy of weight. The contents of the beaker containing the blank were treated with a like amount of acid and transferred to the crucible used as a tare.

As much as possible of the water and acid in both crucibles was evaporated on the steambath. After this the crucibles were partially covered, placed in radiators, and very slowly heated to about 400° C. They were then transferred to a muffle furnace and gradually heated until the nitrate was decomposed, after which they were tightly covered and heated to 1,300° C. The residue obtained in one of two determinations attained constant weight only after it had been heated for 20 hours at 1,300° C. The other did not attain constant weight in 25 hours. This sluggishness in coming to constant weight was attributed to the retention of gases referred to earlier in this paper. In order to determine whether constant weight could be obtained at all, 5 ml of water, 2 ml of sulphuric acid, and 3 ml of hydrofluoric acid were added to the residue and to the blank. The water and acids were evaporated, and the residue was ignited as in the case of the sulphate. Constant weight was obtained by gradually heating to 1,300° C and then igniting at this temperature for 10 hours.

The two results obtained by this procedure are given in table 3, the first of which is included here, even though it was not gotten by simple direct ignition of the nitrate but by the additional treatment with sulphuric and hydrofluoric acids just described. The procedure involving the ignition of the nitrate is not to be recommended.

TABLE 3.—*Results obtained for the atomic weight of gallium by converting the metal to the oxide through the nitrate*

No.	Wt of metal	Wt of Ga_2O_3	Calculated atomic weight
	g	g	
1[a]	0.78420	1.05411	69.73₀
2[a]	.80495	1.08196	69.74₀
			69.73₅=Average.

[a]=first lot of metal.

V. DISCUSSION OF RESULTS

The weights were carefully calibrated by the mass section of the National Bureau of Standards before this work was started and after it was finished, and the proper corrections were made. By the use of a platinum crucible as a counterpoise, the use of brass weights in excess of 4 g was avoided. Errors caused by the effect of changes in humidity on the brass weights were therefore so small that they were entirely negligible.

The balance used was sensitive to 0.05 mg, and yielded weighings reproducible within 0.05 mg. Tests showed that the inequality of the

balance arms could cause a maximum error of only 0.01 mg in any of the determinations. This permitted direct weighing, although a few weighings were made by substitution.

These considerations show that the limit of uncertainty in a single weighing of either the metal or the oxide was 0.05 mg. If the errors were in the same direction in weighing the metal as in weighing the oxide, they were practically without effect, but if they were in opposite directions, errors of considerable magnitude were introduced. In the compound, Ga_2O_3, oxygen constitutes only about one-fourth of the weight, so that in the conversion of metallic gallium to gallic oxide, the relative increase in weight is small. A small error made in weighing the metal or the oxide will, therefore, cause a relatively large error in the calculated atomic weight. For example, in the case of the result, 69.74_5, obtained by converting 1.15767 g of gallium to oxide (no. 1, table 2), if the weight of the metal had been recorded 0.05 mg too high and the weight of the oxide 0.05 mg too low, the calculated atomic weight would have been 69.76_5. If the errors in weighing had been reversed, the calculated atomic weight would have been 69.72_4. This shows that an error of $\pm$ 0.02 can exist in this result, although this is improbable. The smaller weights of gallium were used in the beginning of the work because it was not thought possible to convert the larger quantities of hydroxide or sulphate to oxide without mechanical loss. Later it was found that the conversion of 3.0 g of metal, through either the hydroxide or the sulphate, offered no particular difficulties.

It is evident that the conversion of large amounts of metal to oxide will minimize errors of this kind, and that a weighted average is more reliable than the general average because the former gives added importance to the results obtained by the conversion of large quantities of metal to oxide. The weighted average, 69.73_5, obtained by basing the calculation on the total weight of gallium and the total weight of gallic oxide in the 11 determinations, differs only slightly from the simple general average, 69.73_7. The substantial agreement between this value, 69.73_5, and that of Richards and Craig, 69.720, obtained by an entirely different ratio, not only adds to the reliability of the two values, but it also indicates that no appreciable separation of isotopes occurred in either determination unless the remote assumption is made that such separation could have been practically the same in both cases.

The rounded value for the atomic weight of gallium, based on conversion of the metal to gallic oxide, is 69.74.

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A STUDY FOR THE PREPARATION OF A SPECIFICATION FOR HIGH-EARLY-STRENGTH PORTLAND CEMENT

By G. Rupert Gause

ABSTRACT

This paper reports test results to be used as a basis for the preparation of a Federal specification for high-early-strength cement. Samples of 28 commercial cements were investigated. The cements represented a wide spread in compound composition, fineness, and physical properties.

Four plastic mortars were studied. Both the tensile and compressive strength (2-inch cubes) of each of these mortars varied with the different cements over a considerable range. The rate of setting of these cements was measured by the penetration of 300-g needles, one 1 mm in diameter and one 2 mm in diameter, into the mortars contained in a Vicat ring.

Measurements of length changes were made on 6-inch prisms 1 inch square cured under four different conditions.

The requirements for a specification for high-early-strength cement are discussed and recommendations made for tests to be incorporated into such a specification.

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I. INTRODUCTION

The present study of high-early-strength portland cement was undertaken to obtain data from which a Federal specification could be prepared. Shortly prior to the starting of this work the American Society for Testing Materials had issued a proposed tentative method of test for compressive strength of portland-cement mortar. This method, since adopted as Tentative Method C 109–34T,[1] requires a 2-inch test cube made from a plastic mortar of fixed proportions. It was decided to include in the present investigation studies on this particular plastic mortar, together with other mortars of different proportions, as well as tests for compliance with the Tentative Specifications for High-Early-Strength Portland Cement (C 74–30) of the American Society for Testing Materials.[2]

[1] Proc. Am. Soc. Testing Materials 34 part I, p. 743 (1934).
[2] Proc. Am. Soc. Testing Materials 30 part I, p. 1,016 (1930).

II. MATERIALS AND STORAGE CONDITIONS

Samples of 28 commercial high-early-strength cements in approximately 25-pound lots were obtained from manufacturers, whose cooperation is hereby gratefully acknowledged. Those few cements which were not received in airtight containers were placed in such containers shortly after their arrival. Before testing, each cement was put through a no. 20 sieve to remove any lumps or foreign matter.

Both standard Ottawa sand, meeting the requirements of Federal Specification SS–C–191, and a graded Ottawa sand were used in the tests. The graded sand had the following sizing: 99 percent retained on the no. 100 sieve, 70 percent on the no. 50, 1 percent on the no. 30 and none on the no. 16.

Tap water at 21±2° C was used for mixing. The temperature of all dry materials at time of mixing was 21±2° C. The air of the laboratory for mixing, molding, and air storage was maintained at a temperature of 21±2° C and at a relative humidity of 60±5 percent, and the air of the moist cabinet at the same temperature, but at a relative humidity of 95 percent or higher. The storage tanks contained water at 21±3° C.

III. DESCRIPTION OF TESTS

A chemical analysis was made of each cement, and the specific surface and distribution of particle size, using the Wagner turbidimeter, were determined.

Tests were made for compliance with the requirements of Federal Specification for Portland Cement, SS–C–191, with tensile strength tests made at 1 and 3 days in addition to the required 7- and 28-day tests. However, the no. 200 sieve fineness was determined by a wet method. A 10-g sample was placed in a certified no. 200 full-height sieve, the sample thoroughly wetted by slowly pouring water into the sieve, and then washed for 1 minute by holding sieve and sample under a spray nozzle. The nozzle contained seventeen 0.02-inch holes and the water was maintained at a nozzle pressure of 15 lb/in.^{2} The sieve with residue was then placed for a period of 15 minutes in an electric oven maintained at 105 to 110° C. The sieve was then removed from the oven, allowed to cool, and the residue weighed.

Four plastic mortars were studied:

Mortar A was proportioned 1 part of cement to 2.75 parts by weight of graded Ottawa sand, and had a C/W (cement/water, by weight) ratio of 2.0. The proportion of cement and sand was almost exactly as specified by the American Society for Testing Materials in its tentative method C 109–34T, but the C/W ratio was slightly larger.

Mortar B was proportioned the same as mortar A, and the water content adjusted, as shown in table 3, to give a flow of 100 to 110 on the 10-inch flow table.

Mortar C had a C/W ratio of 2.0, the sand content being adjusted, as shown in table 3, to give each mortar such a consistency that it had a flow of 100 to 110. This flow was the same as for mortar B and the C/W ratio the same as for mortar A.

Mortar D was proportioned 1 part of cement to 2.77 parts by weight of graded Ottawa sand, and had a C/W ratio of 1.88. These

are the proportions required by ASTM Tentative Method C109–34T.

On each of the mortars A, B, and C the following tests were made:

1. Strength tests for both tension and compression (2-inch cubes) were made at 1, 3, 7, and 28 days.

In addition, on mortar D, strength tests for tension and compression at 1 and 3 days were made on those cements of which sufficient material was available.

2. Immediately after mixing, a mortar was placed in a Vicat ring resting on a glass plate, the top troweled level, and the specimen placed under a 100-g Vicat plunger 10 mm in diameter, which was brought into contact with the top of the mortar and released exactly 45 seconds after completion of the mixing. The depth of penetration of the plunger in 30 seconds was a measure of consistency.

3. The depth of penetration of a standard (1 mm) Vicat needle weighing 300 g and also of a 2-mm needle of the same weight was determined, as a measure of time of set at half-hour intervals until less than 1-mm penetration was obtained. The specimens were made in duplicate.

4a. Two pats 3 inches in diameter by ½ inch in height were formed from each mortar on glass plates and cured in the moist cabinet for 24 hours, then in steam at 98° to 100° C for 5 hours, and observed for signs of shrinkage, disintegration, or warping. One pat was then stored in water at 21° C and one in laboratory air, and each was examined at the age of 7, 14, and 28 days.

4b. The length changes of 1- by 1- by 6-inch prisms were measured after they had been cured for 24 hours in the moist cabinet and then cured under one of the following four conditions:

1. Five hours in steam at 98° to 100° C, then cooled to 21°, and then stored in air at 21° and readings made at 7, 14, and 28 days.
2. Five hours in steam, then cooled to 21° C, and then stored in water, and readings made at 7, 14, and 28 days.
3. Stored in air, and readings made at 7, 14, and 28 days.
4. One hour in saturated steam at 100 lb/in.^{2} gage pressure, then cooled.

The mixing of all plastic mortars, as called for by the proposed method, was done in a vitreous enamel ware bowl of about 1-gallon capacity. The bowl was wiped with a damp cloth, the water poured into it, then the cement was added and mixed with the water for 30 seconds with one hand, then approximately one-half of the sand was added and the mixing continued for another 30 seconds. The remainder of the sand was then added and the mixing continued for 90 seconds. As soon as the mixing was completed the flow-table mold, which had previously been wiped dry and clean, was half filled and puddled, then filled to the rim and puddled, and the surface scraped off with a trowel. The mold was removed and the table given 25 one-half inch drops in 15 seconds. The flow was the increase in the diameter of the mortar expressed as a percentage of the original diameter.

Briquet and cube molds were greased with a thin film of light cup grease, then placed on a plane brass plate similarly greased and the contacts sealed with a molten mixture of 5 parts of rosin to 3 parts of paraffin, by weight. In molding the briquets and cubes the molds were half filled and puddled with the finger tips, then filled and the puddling repeated. The excess mortar was then scraped off and the tops troweled just enough to secure a smooth surface flush with the top of the mold. Immediately after molding, the specimens were placed in the moist cabinet. They were removed from the molds 23 to 24 hours after making. Those for later ages were placed in water immediately upon their removal from the molds and kept there until tested. The briquets were all tested with the same tensile machine of 1,000-pound capacity. The cubes of cements 1 to 8 were tested with a screw-type machine and the others with a hydraulic machine. Cubes tested with the hydraulic machine were loaded at the rate of 3,000 pounds per square inch per minute.

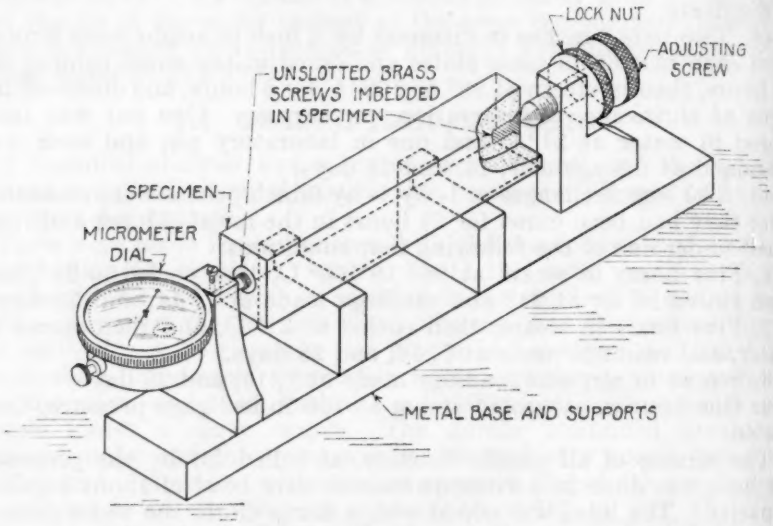

FIGURE 1.—*Apparatus for measuring the length of prisms.*

The prisms were molded with a special flathead brass screw ½ by 3/16 inch in each end. The unslotted screw heads served as reference planes for the length measurements. The molds were filled in the same manner as the cube molds, care being taken to fill completely the ends of the molds around the screws. Immediately after molding, the specimens were placed in the moist cabinet and at the end of 24 hours removed from the molds. The length of each prism was then measured to the nearest 0.0001 inch with the apparatus shown in figure 1. Two readings were made on each specimen, reversing the prism for the second reading. Four sets of 3 prisms were made from each mortar and cured as described above.

TABLE 1.—*Oxide analysis, compound composition and particle size*

Cement	Oxide analysis, in percent by weight							Ignition loss, in percent by weight	Insoluble residue, in percent by weight	Computed compound composition,[a] in percent by weight						Particle size						Surface area cm²/g
																Cumulative percent finer than—						
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	"Free lime"			C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	"Uncombined CaO"	7.5 μ	20 μ	30 μ	40 μ	50 μ	60 μ	
1	20.8	2.0	5.7	64.5	3.7	2.2	0.9	1.2	0.1	57	17	12	6	3.7	0	30.6	74.4	90.2	94.9	99.3	99.3	2,450
2	19.6	2.2	6.3	62.8	3.9	2.3	0.5	3.1	0.2	55	15	13	7	3.9	0	41.7	65.2	80.6	89.8	94.6	96.4	2,680
3	21.0	2.9	5.3	63.2	3.2	2.2	0.4	2.0	0.2	51	22	9	9	3.7	0	35.5	63.9	78.6	87.7	92.7	96.1	2,420
4	19.9	2.8	7.3	62.7	2.8	2.4	0.8	1.6	0.2	44	24	15	9	4.1	0	38.5	64.4	79.6	88.0	93.0	97.0	2,650
5	19.2	2.4	7.3	63.3	2.9	2.3	0.4	2.7	0.1	53	15	15	7	3.9	0	24.6	66.1	83.2	93.1	95.9	98.3	2,190
6	19.5	2.3	5.7	66.0	2.2	2.2	1.1	2.2	0.2	73	1	11	7	3.7	0	24.4	58.0	73.6	82.5	88.4	92.7	1,990
7	20.9	3.2	4.5	64.1	4.0	2.3	1.5	1.2	0.2	61	14	7	10	3.9	0	28.6	60.7	72.5	85.4	89.8	93.9	2,220
8	20.1	2.8	5.4	66.0	1.7	2.1	0.3	1.7	0.2	70	5	10	9	3.6	0	27.7	64.2	82.1	92.9	98.3	98.3	2,250
9	20.1	3.3	5.7	65.9	2.5	1.8	1.0	1.2	0.1	67	7	10	10	3.1	0	34.7	61.1	77.0	85.7	92.2	95.5	2,380
10	20.3	3.7	6.6	63.1	1.4	2.3	0.8	2.4	0.2	46	23	11	11	3.9	0	36.5	68.5	84.1	93.3	98.3	98.3	2,520
11	19.6	3.4	6.7	65.9	1.0	2.5	0.8	1.0	0.1	62	9	12	10	4.2	0	29.0	54.1	66.5	75.4	82.6	89.2	2,070
12	21.1	2.7	5.8	63.2	2.7	2.7	0.9	1.8	0.3	46	25	11	8	4.6	0	34.1	66.6	85.3	93.0	98.0	98.0	2,480
13 [b]	19.2	2.7	7.0	64.8	1.6	2.2	2.6	2.0	0.3	61	9	14	8	3.7	0	30.1	55.8	73.4	83.4	90.8	96.1	2,170
14	19.9	3.1	6.9	65.0	1.4	2.3	1.8	1.3	0.1	56	15	13	10	3.9	0	34.5	60.6	75.4	83.8	88.8	94.9	2,390
15	19.4	2.3	5.1	66.4	1.6	2.5	3.5	2.1	0.1	74	0	10	7	4.2	1.2	31.7	56.1	75.2	85.2	93.2	96.5	2,190
16	18.7	2.4	7.0	63.6	3.5	2.3	0.6	1.9	0.1	60	9	15	7	3.9	0	27.5	54.4	70.3	80.5	91.6	95.8	2,130
17	19.4	3.0	6.3	65.7	1.8	2.1	1.1	1.4	0.1	67	5	12	9	3.6	0	27.8	51.1	72.2	85.9	91.1	96.2	2,000
18	18.6	3.0	7.5	65.8	0.9	2.3	0.3	1.5	0.1	65	4	15	9	3.9	0	28.6	58.8	72.6	84.7	90.7	95.1	2,120
19	19.0	1.9	6.5	67.5	0.9	2.2	1.6	1.6	0.2	72	0	14	6	3.7	1.3	36.2	64.1	78.2	86.2	92.4	95.7	2,360
20	18.0	2.4	4.9	64.4	3.7	2.4	6.4	3.6	0.3	68	0	9	7	4.1	3.4	42.6	72.9	87.6	92.2	98.0	98.0	2,740
21	20.8	2.9	5.9	63.7	2.0	2.4	0.9	2.1	0.5	51	21	11	9	4.1	0	40.9	69.1	84.4	91.0	97.2	97.2	2,640
22	19.2	3.4	6.3	63.6	3.6	2.5	1.0	1.5	0.2	59	11	11	10	4.2	0	34.7	62.5	75.7	85.9	92.8	95.5	2,260
23 [c]	21.0	2.2	5.1	62.8	3.8	2.5	0.9	2.4	0.2	52	21	9	7	4.2	0	43.8	69.4	85.1	92.2	95.8	98.0	2,860
24	19.9	3.1	6.4	64.2	2.1	2.5	2.0	1.5	0.2	55	16	12	10	4.2	0	31.0	70.7	81.4	90.9	95.5	98.2	2,350
25	20.0	4.2	6.2	64.1	1.5	2.7	0.8	1.4	0.2	54	17	9	13	4.6	0	36.0	66.8	84.8	92.8	98.2	99.6	2,460
26	22.9	1.7	4.1	66.7	2.0	1.9	1.0	1.1	0.2	62	19	8	5	3.2	0	32.7	62.1	77.1	85.5	91.7	96.2	2,350
27	21.3	2.5	5.5	64.5	1.7	2.5	1.0	1.4	0.4	53	21	10	8	4.2	0	36.3	56.5	70.4	79.0	86.4	93.0	2,420
28	19.4	3.6	6.1	65.5	0.7	2.1	2.9	2.2	0.2	67	5	10	11	3.6	0	34.1	59.9	74.6	84.7	89.1	95.2	2,380
Average										59	12	11	8	3.9								2,361
Maximum	22.9	4.2	7.5	67.5	4.0	2.7	6.4	3.6	0.5	74	25	15	13	4.6		43.8						2,860
Minimum	18.0	1.7	4.1	62.7	0.7	1.8	0.3	1.0	0.1	44	0	7	5	3.1		24.4						1,990

[a] $C_3S = 3CaO.SiO_2$
$C_2S = 2CaO.SiO_2$
$C_3A = 3CaO.Al_2O_3$
$C_4AF = 4CaO.Al_2O_3.Fe_2O_3$

[b] 0.4 percent of FeO.
[c] 0.2 percent of FeO.

TABLE 2.—*Mortar strengths (pounds per square inch)*

Cement	1:3 Standard Ottawa sand mortar[a]				Mortar A[b]								Mortar B[b]								Mortar C[b]								Mortar D[b]			
	Tensile strength				Tensile strength				Compressive strength				Tensile strength				Compressive strength				Tensile strength				Compressive strength				Tensile strength		Compressive strength	
	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	7 day	28 day	1 day	3 day	1 day	3 day
1	265	350	420	495	215	335	375	490	1480	3120	4220	5850	185	300	420	440	1260	3000	4520	5550	210	330	445	520	1720	3220	4850	5850	[d]185	[d]300	[d]1260	[d]3000
2	280	405	480	495	235	315	420	470	1780	3450	4720	6050	205	330	420	465	1510	3100	4600	5850	265	360	470	535	2140	4100	5350	7150				
3	220	365	420	505	190	265	350	500	1080	3000	4600	5700	165	245	330	485	930	2950	4520	5950	185	350	415	505	1180	3250	4850	6550	130	280	1040	2600
4	280	390	435	445	205	335	405	495	1380	3020	4350	5950	175	330	350	455	940	2600	4070	5800	215	370	460	510	1520	3350	5250	7150			1280	
5	305	410	450	450	205	325	385	440	1300	3400	3950	4250	195	295	360	445	1070	2800	3700	4550	210	330	395	450	1410	4020	4720	6150				
6	290	390	445	425	220	345	425	505	1410	3600	4870	6020	160	340	450	525	1140	3400	4920	5950	220	390	495	530	1660	4500	6300	7500	170	325	1380	3900
7	295	360	420	500	245	335	370	445	1820	2900	3720	4950	205	275	355	450	1220	2320	3500	5070	245	355	450	495	1770	3400	4450	6250			2010	
8	275	335	380	350	220	330	420	455	1570	3020	4020	4900	210	310	420	435	1430	2800	4050	5150	225	355	445	480	1740	3420	4900	5800	[d]210	[d]310	[d]1430	[d]2800
9	210	350	390	455	175	290	335	455	1030	2350	4120	5300	160	275	360	410	970	2320	3600	5250	170	285	405	485	1140	2670	4470	6050	[d]160	[d]275	[d]970	[d]2320
10	280	390	460	495	205	345	360	460	1400	3520	4650	6150	160	310	360	460	1040	2870	4000	5850	220	395	410	505	1490	3620	5650	7300				
11	265	370	410	500	185	310	420	445	1450	2800	3870	5050	170	285	375	405	1200	2550	3650	4950	205	335	445	495	1830	3500	5150					
12	280	400	470	460	230	320	420	505	2060	3320	4700	6100	200	300	400	495	2050	2720	3800	5600	280	360	415	540	2260	3820	5770	7000			1420	2750
13	265	400	455	430	205	330	405	440	1710	3220	4870	5800	180	260	370	395	1220	2600	4320	5150	245	330	410	500	1700	3800	5470	6550	180	330	1370	3070
14	305	405	475	460	215	380	410	435	1660	3670	5350	6250	165	290	390	435	1170	2920	4520	6100	220	355	425	510	1700	4020	5950	7450	215	350	1300	3270
15	285	395	440	425	240	310	445	435	1970	3350	4800	6000	240	340	415	470	1560	3200	5000	6000	320	390	555	535	2290	4820	6600	7950	230	360	1810	4200
16	300	365	430	475	200	335	405	465	1620	3400	4570	5850	155	285	370	425	1280	2770	3800	5550	240	375	450	500	1900	3850	5550	7050	200	330	1330	3250
17	280	385	435	460	225	345	415	455	1820	3620	4820	5750	180	315	385	440	1400	3120	4570	5500	260	380	435	480	1970	4070	5420	6450			1630	
18	290	395	445	465	240	365	430	495	1860	4120	6300	7020	195	365	390	445	1430	3520	5150	6150	280	405	475	515	2190	4520	6420	7600	205	365	1630	4050
19	315	385	415	465	290	355	415	435	2040	4370	5420	5720	230	345	440	430	1700	3700	4800	5320	325	405	525	495	2110	4800	6320	7100	260	380	1910	3720
20	325	385	430	445	245	345	405	465	2230	3950	5100	6120	190	310	355	460	1890	3500	4650	5500	245	385	445	480	2030	3870	5400	6950	205	315	1830	3420
21	255	290	310	385	180	275	320	390	1260	2920	3720	5150	150	270	310	400	1060	2450	3600	4800	175	320	350	405	1420	3270	3400	5400				
22	305	375	440	470	220	380	425	465	2020	3420	4900	6250	185	295	410	445	1500	2820	4350	5400	260	410	505	540	2130	4170	5550	7600				
23	255	330	395	415	170	300	375	455	1210	2900	4700	6150	155	270	340	445	1010	2650			180	305	415	505	1440	3400					1260	
24	305	410	475	460	250	340	410	480	1830	3670	4950	6250	210	310	400	450	1500	3350	4620	6000	245	380	460	505	1850	4120	5120	6750			1660	
25	320	400	475	525	235	410	425	480	1400	3670	4500	5650	190	375	435	495	1250	3200	4620	5900	245	405	440	475	1540	4220	5200	6750	215	390	1480	3620

26	255	400	440	490	235	365	450	520	2130	3470	4570	6900	240	320	460	480	1930	3320	4470	7100	240	355	460	535	2190	3600	5170	7400	205	280	1750	3100
27	255	320	310	375	195	265	325	435	1190	2470	3270	4350	195	265	325	435	1190	2470	3270	4350	195	265	325	435	1190	2470	3270	4350	190	255	1020	1970
28	305	410	455	445	210	385	455	520	1720	3970	5650	7100	200	375	430	495	1570	3970	5600	6900	220	400	490	510	1820	4270	5750	7600	-----	-----	-----	-----
Average	281	377	429	456	217	332	400	466	1620	3350	4620	5810	187	306	386	450	1340	2960	4310	5600	234	360	443	500	1760	3790	5270	6760	200	330	1500	3300
Maximum	325	410	480	525	290	410	455	520	2230	4370	6300	7100	240	375	460	525	2050	3970	5600	7100	325	410	555	540	2290	4820	6600	7950	260	390	2010	4200
Minimum	210	290	310	350	170	265	320	390	1030	2350	3270	4250	155	245	310	395	930	2320	3270	4350	170	265	325	405	1140	2470	3270	4350	130	255	970	1970
Uniformity[c]	6.0	4.7	3.7	5.8	4.8	6.5	5.8	4.6	3.5	3.8	3.5	3.8	5.2	4.6	5.0	5.1	4.2	3.2	4.1	3.7	5.8	4.2	5.8	4.8	3.3	3.0	4.8	4.2	7.6	5.3	3.0	3.6

[a] Mortar of the consistency and proportion required in Federal Specification SS–C–191 for portland cement.

[b] The proportions by weight of cement and graded Ottawa sand and the C/W ratio, by weight, or the flow of the mortars are as follows:

Mortar A. 1:2.75, C/W = 2.0.
Mortar B. 1:2.75, flow = 100 to 110.
Mortar C. 1:X, C/W = 2.0.
flow = 100 to 110.
Mortar D. 1:2.77, C/W = 1.88.

The grading of the sand is as follows:

Amount retained on sieve no.—	*Percent*
16	0
30	1
50	70
100	99

[c] Standard deviation of specimens made from the same batch expressed in percent.

[d] Same specimens for mortars B and D.

IV. RESULTS OF TESTS

In table 1 are given the chemical analysis, the compound composition computed by the method as given by Bogue,[3] the specific surface, and the distribution of particle size for each cement. In calculating the amounts of the compounds the "free CaO" has been neglected because of the inability to distinguish between CaO, uncombined in the clinker from which the cement was made, and $Ca(OH)_2$ resulting from the hydrolysis of the cement during processing and storage. It is of interest to note that the "free-lime" content of the cements varied up to 6.4 percent. The cements varied through a wide range of composition. One cement had a C_3S content of 74 percent and zero C_2S content, while at the other extreme was a cement with a C_3S content of 46 percent and a C_2S content of 25 percent. The C_3A content varied from 7 to 15 percent. Two cements exceeded the sulfuric-anhydride limit of 2.5 percent specified in ASTM Tentative Specification C74–30T.

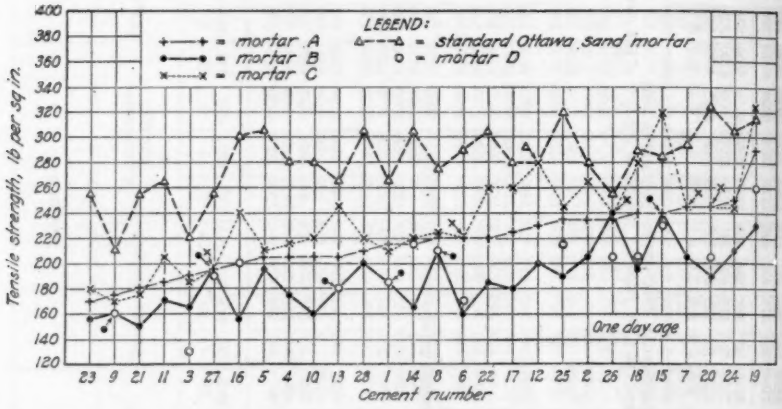

FIGURE 2.—*One-day tensile strengths of plastic- and standard-sand mortars.*

The specific surfaces ranged from 1,990 to 2,860 cm^2 per g. Normal portland cements have specific surfaces ranging from about 1,400 to 2,000 cm^2 per g.

In table 2 are given the results of the strength tests. Each value is the average of tests on 3 specimens made from 1 batch. Nine cements failed to meet the strength requirement of 275 lb/in.^{2} at 1 day and 10 failed to meet that of 375 lb/in.^{2} at 3 days, as specified in the ASTM tentative specification.

The standard deviations were computed from the formula

$$\sigma = \sqrt{\frac{\Sigma v^2}{2N}}$$

where v=deviation of each individual break from the average of three expressed as a percentage of that average, and N is the number of groups of three. These deviations, which give a measure of the uni-

[3] R. H. Bogue, Calculation of Compounds in Portland Cement, Portland Cement Association Fellowship Paper 21.

formity of tests on specimens made from the same batch, show that the compressive tests were consistently more uniform than the tensile tests. The deviations of the briquet strengths are approximately 50 percent greater than those of the compressive strengths. No one mortar shows a superiority in uniformity over another, nor does there seem to be an appreciable difference between the plastic-mortar briquets and the standard Ottawa sand briquets.

Figure 2 gives the 1-day tensile strengths of each cement for the different mortars, figure 3 the 1-day compressive strengths, figure 4 the 3-day tensile strengths, and figure 5 the 3-day compressive strengths. In each case the cements were arbitrarily plotted in the order of the strengths of mortar A. These graphs portray some interesting facts. For most cements the strengths of mortars C and B lie respectively, above and below those of mortar A. In general, those cements having high tensile strength have also high compressive strength and those having low tensile strength have also low compressive strength.

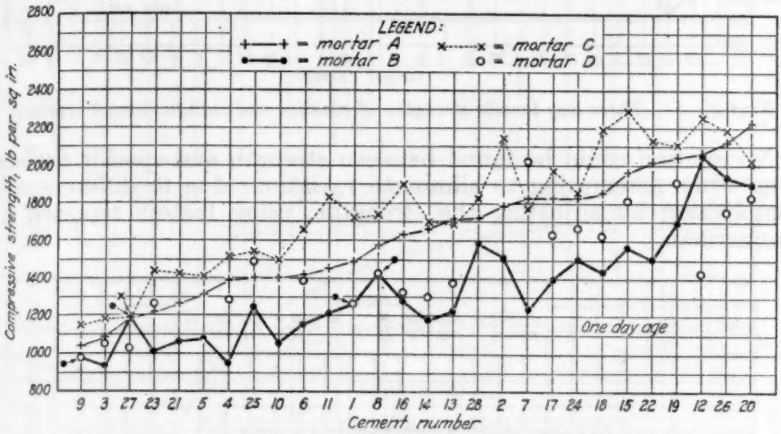

FIGURE 3.—*One-day compressive strengths of plastic mortars.*

The strength scales were so chosen that each unit on the compressive scale represents the same percentage of the average compressive strength as each unit on the tensile scale represents in percentage of the tensile strength. The figures show that the compressive strengths rise much more sharply going from left to right than do the tensile strengths. Therefore, the percentage spread in compressive strength for this group of cements is greater than is the percentage spread in tensile strength.

Figures 2, 3, 4, and 5 show that decreasing the C/W ratio, as in mortar B relative to mortar A, results in a decrease in strength and that increasing the cement-sand ratio, as in mortar C relative to mortar A, causes an increase in strength. That is, adjusting the C/W ratio and the cement-sand ratio to secure the same flow acts upon the strength in opposite directions.

The average tensile strength of mortar A with respect to age is plotted in figure 6 (a) and the compressive strength in figure 6 (b). The change in strength at 24 hours is about 3.1 percent per hour for tensile and 3.3 percent per hour for compressive, and at 72 hours the change is 0.3 percent per hour for tensile, and 0.5 percent per hour

for compressive. These percentages are only approximate, but will not vary appreciably for the different mortars or cements. It is evident that 24-hour tests should be made as near 24 hours as possible and that 72-hour tests should be made within an hour of 72 hours.

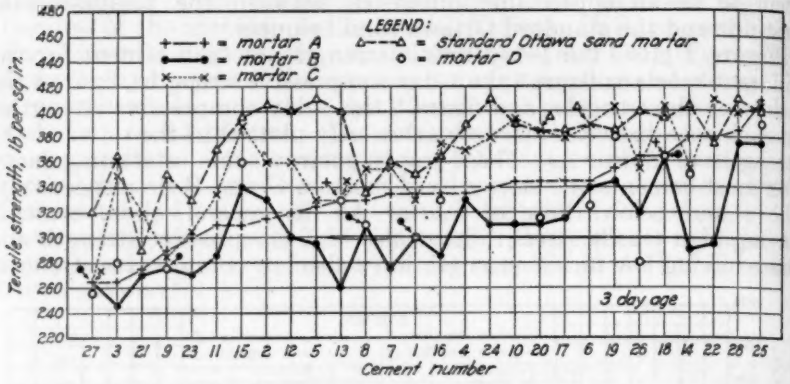

FIGURE 4.—*Three-day tensile strengths of plastic- and standard-sand mortars.*

No relation could be found between strength and specific surface, even when attempting to eliminate variations due to differences in composition by adjusting the strengths, using factors reported by Gonnerman.[4]

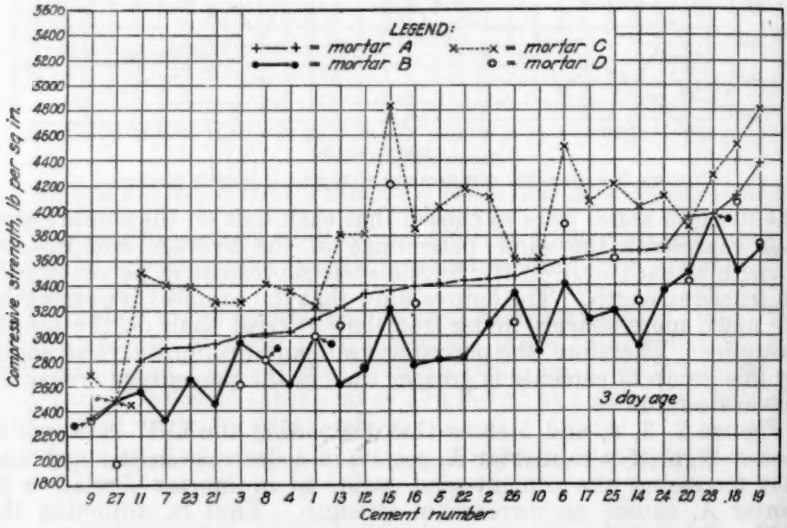

FIGURE 5.—*Three-day compressive strengths of plastic mortars.*

In table 3 are given the proportions and consistencies of mortars A, B, and C, as measured by both flow table and 100-g plunger. The values show that the penetration measurements were much less sensitive than the flow measurements to both changes in C/W ratio

[4] Proc. Am. Soc. Testing Materials 34, part II, 287 (1934).

and cement-sand ratio. The table also shows that, with the exception of cements nos. 1 and 25, the penetrations into mortar C were greater than those into mortar B, and since these two mortars were

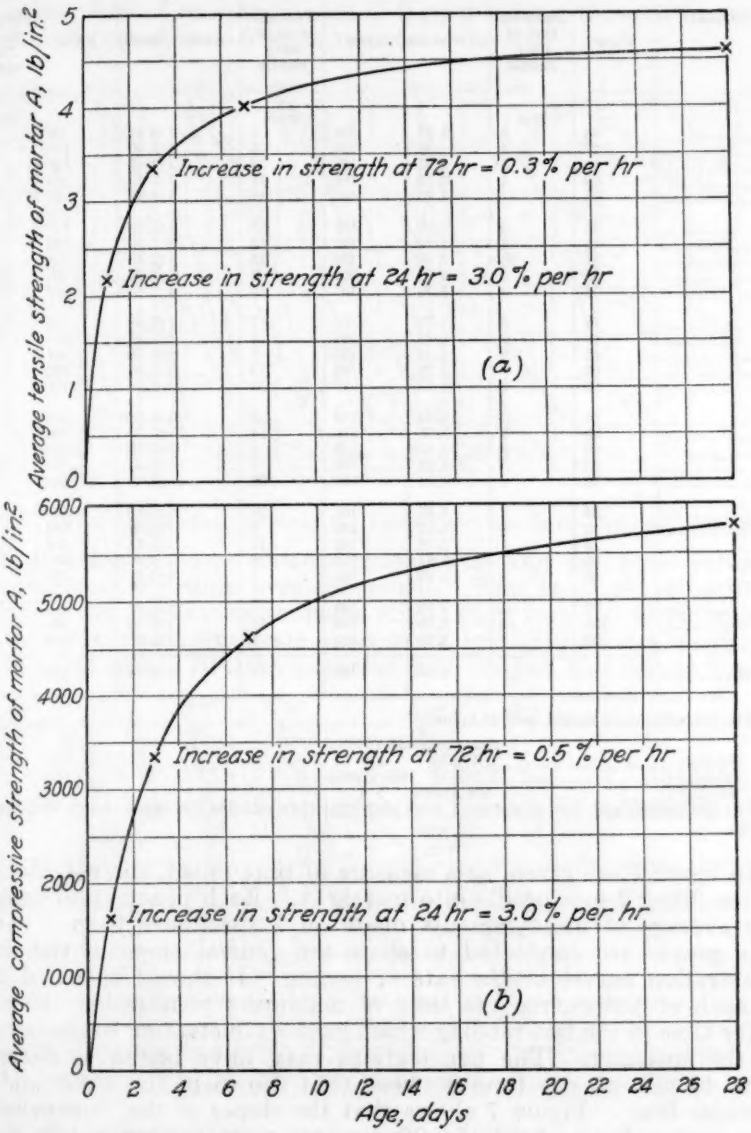

FIGURE 6.—*Relation between strength of plastic mortars and age.*

gaged to an approximate common flow, it seems that the penetration measurements are more sensitive to a change in flow produced by varying the cement-sand ratio than they are to the same change in flow produced by varying the C/W ratio.

TABLE 3.—*Consistency of Plastic Mortars*

Cement	Mortar A [a]		Mortar B [a]			Mortar C [a]		
	Flow	Penetration of 100-g needle	C/W ratio	Flow	Penetration of 100-g needle	Cement: sand	Flow	Penetration of 100-g needle
		mm			mm			mm
1	78	3	1.87	104	6	1:2.55	100	5
2	73	4	1.85	100	8	1:2.40	105	10
3	88	5	1.92	100	12	1:2.55	105	13
4	73	3	1.78	105	17	1:2.40	104	18
5	75	4	1.82	100	12	1:2.40	107	14
6	74	2	1.78	109	11	1:2.40	109	15
7	65	4	1.72	110	13	1:2.30	108	33
8	81	11	1.88	104	15	1:2.55	105	33
9	83	5	1.88	100	9	1:2.50	107	23
10	75	4	1.78	107	13	1:2.42	107	17
11	74	4	1.78	101	7	1:2.45	100	8
12	67	2	1.75	108	8	1:2.35	104	14
13	65	2	1.75	100	8	1:2.30	104	14
14	62	3	1.72	106	10	1:2.26	105	18
15	62	3	1.72	110	11	1:2.30	109	20
16	64	2	1.75	104	5	1:2.26	106	19
17	65	2	1.75	110	14	1:2.32	110	26
18	60	2	1.75	100	6	1:2.30	100	10
19	62	2	1.75	109	7	1:2.32	107	10
20	79	4	1.85	104	25	1:2.40	104	30
21	84	5	1.85	100	28	1:2.50	100	30
22	59	3	1.72	101	9	1:2.24	104	18
23	75	4	1.78	101	14	1:2.42	100	27
24	81	7	1.85	101	14	1:2.48	109	19
25	80	3	1.82	105	7	1:2.48	103	7
26	91	5	1.92	103	7	1:2.58	102	10
27	105	15	2.00	105	[b] 15	1:2.75	105	[b] 15
28	92	5	1.92	100	7	1:2.56	110	9
Avg	75	4	1.80	104	11	1:2.41	105	17

[a] The proportions by weight were as follows:

	Cement: sand	*C/W*
Mortar A	1:2.75	2.0
Mortar B	1:2.75	See above
Mortar C	See above	2.0

[b] The proportions and flow of mortar A were such that they satisfied the requirements of mortars B and C.

In figure 7 are given, as a measure of time of set, the penetrations of the 300-g 2-mm needle into mortar A. Each penetration value is the average of measurements made on 2 specimens from 1 batch. The points are connected to show the general slope of the time-penetration curves or the rate of setting. It should be noted that in each of the curves the time of maximum penetration (40 mm) is the time of the last reading which gave a penetration to the bottom of the specimen. The penetrations may have begun to decrease from 40 mm at any time between that shown in the curve and 30 minutes later. Figure 7 shows that the slopes of the time-penetration curves for each of the 28 cements were approximately alike. Figure 8 shows the same similarity of slopes in the time-penetration curves for the 300-g 1-mm needle. The order of the cements according to the position of their curves in figure 8 is approximately the same as the order according to the position of their curves in figure 7. We see, therefore, that if we determine a condition of set by a definite penetration, the cements will have about the same relative order of

time of setting, no matter what particular penetration value we choose or which needle we consider.

Similar data on mortars B and C gave curves of the same form as those in figures 7 and 8, the only systematic difference being that the penetrations of mortars B and C lagged behind those of mortar A by an interval of from 0 to 30 minutes.

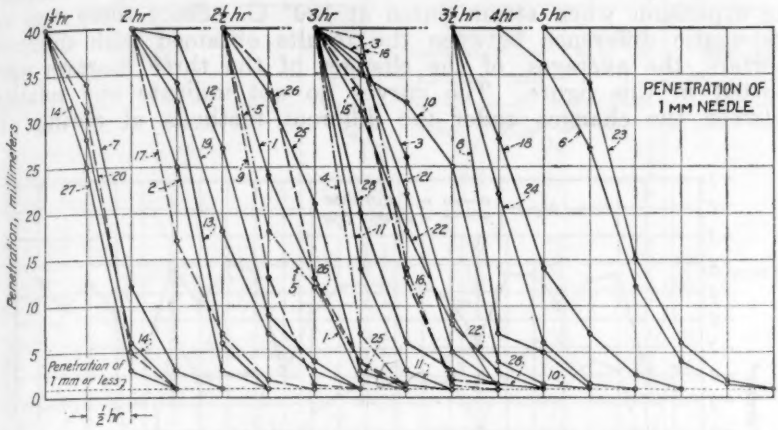

FIGURE 7.—*Time-penetration curves of the 2-mm Vicat needle for different cements.*

The precision of these determinations was poor as far as actual penetrations at any time were concerned. That is, at say 4 hours, repeat tests on the same specimens might vary from 10 to 20 mm, and check tests on a duplicate specimen might give results varying from 15 to 25 mm. But the precision with respect to time, at least

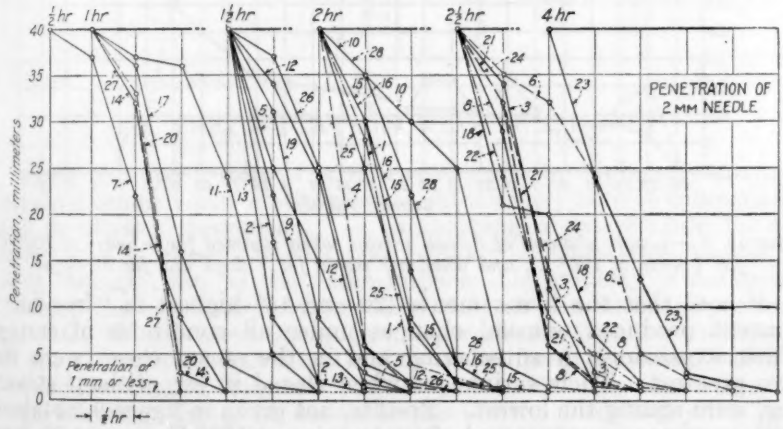

FIGURE 8.—*Time-penetration curves of the 1-mm Vicat needle for different cements.*

during the initial setting period, was well within a 30-minute period. That is, on duplicate test specimens the readings of one specimen never lagged behind those of the other by as much as 30 minutes.

In table 4 are given the results of the tests for time of set, fineness, and soundness, when made according to the requirements of the

Federal specification for portland cement. All cements satisfactorily met the requirements for time of set, soundness, and fineness, of the Federal specification and the ASTM Tentative Specification C 74–30T.

In figure 9 are shown the length changes of three sets of specimens, the first of which was steam cured at 100° C for 5 hours, the second steam cured at 170° C for 1 hour, and the third air stored, without steam curing. The cements were plotted in the order of increasing expansion when steam cured at 100° C. Since there was no systematic difference between the results obtained with different mortars, the averages of the changes of the three mortars were plotted in this figure. The curves do not indicate any relation between the changes under the different methods of curing. It

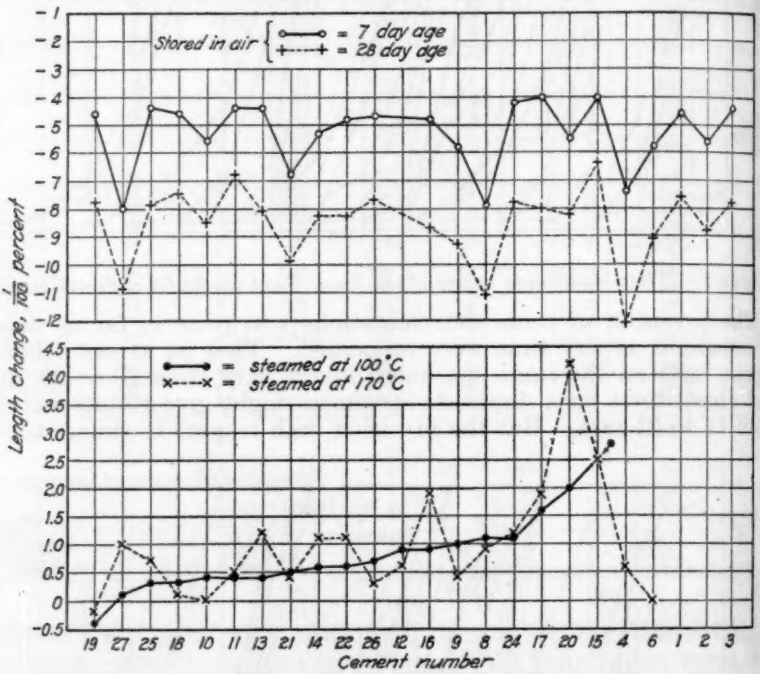
Stored in air
= 7 day age
= 28 day age
= steamed at 100°C
= steamed at 170°C
Length change, per percent
Cement number
19 27 25 18 10 11 13 21 14 22 26 12 16 9 8 24 17 20 15 4 6 1 2 3

FIGURE 9.—*Length changes of 6-inch prisms when steamed for 5 hours at 100° C, for 1 hour at 170° C, and when air stored for 7 days and for 28 days.*

is of note that the two cements (20 and 15) highest in "free-lime" content produced unusual changes under all conditions of curing. Their expansions in autoclaving and in the steam closet were the two greatest. Their shrinkages when stored in air, without steaming, were among the lowest. Results, not given in figure 9, obtained with specimens water stored after steaming at 100° C, gave at 28-days age an average expansion for all cements of 1.9 percent, with cements 20 and 15 as extremes with 3.9 and 5.1 percent, respectively. Specimens air stored, after steaming at 100° C, gave at 28-days age an average contraction of 3.5 percent, with cements 20 and 15 as the two lowest with 1.9 and 0.8 percent, respectively. Although no visual signs of unsoundness were observed in any of the prisms or mortar pats,

these unusual length changes of the two cements highest in "free lime" cannot but cast a shadow of doubt on the question of their soundness.

TABLE 4.—*Fineness, soundness, and time of set*

Tests according to methods of Federal Specification for portland cement SS-C-191. The cements were all sound.

Cement	H_2O for normal consistency	Time of set		Residue on no. 200 sieve	Remarks
		Initial	Final		
	%	*Hours*	*Hours*	%	
1	28.0	2¾	5¼	0.5	
2	24.4	1½	3¼	1.8	
3	26.0	3¼	4¾	1.3	
4	25.6	2	4	1.1	
5	25.6	2½	4¼	0.2	
6	24.2	2¾	5¾	2.4	
7	26.6	2	4¼	2.4	(1).
8	25.6	2¾	4¾	0.3	Waterproofed.
9	24.4	2¼	4½	1.6	(1).
10	25.0	2¾	5¾	0.7	
11	24.4	1¼	4¾	4.6	(1).
12	26.8	2½	4¼	0.5	
13	26.0	2	3½	0.9	(1).
14	25.0	1¼	3	1.9	
15	25.0	2½	4¾	1.0	
16	24.8	2¼	4½	0.9	
17	24.4	2	3½	0.7	
18	25.8	3¾	6	1.0	
19	26.0	2½	4½	0.9	
20	25.6	1¼	3¼	0.7	
21	27.0	2¾	4¾	0.8	Waterproofed.
22	24.4	2½	4½	1.4	
23	27.0	3¾	7	0.6	Waterproofed.
24	25.8	4	6	0.2	
25	26.6	2	4	0.1	
26	25.0	2½	4¾	1.7	
27	25.4	1½	3½	1.8	
28	24.0	1¾	3¾	1.6	

[1] Stiffened up immediately after mixing.

V. SPECIFICATION REQUIREMENTS

From the test results it is apparent that the high-early-strength portland cements now on the market differ widely both in composition and in physical properties. In establishing a specification for the acceptance of these cements, the primary consideration should be early strength, for, as the name implies, this property is the distinguishing characteristic between these cements and standard portland cements. The present investigation has shown that the uniformity of the strength of individual cubes made from the same batch is better than that of briquets.

In selecting the most desirable mortar the foregoing data have little to offer. It does seem that the most satisfactory mortar would be one whose C/W ratio was determined by some measure of consistency. But the difficulties of such a measure are well known. From other investigations there does not seem to be satisfactory agreement between flow-table measurements made by different laboratories. The Vicat needle, which appears from this investigation to be less sensitive than the flow table, has also the disadvantage of poor pre-

cision among repeat tests on identical specimens. It seems that until some satisfactory method can be found for determining the C/W ratio, the best selection of a mortar would be one of fixed proportions and C/W ratio, such as mortar A or mortar D. Mortar A was, as a rule, too harsh for ease of placement in the molds. The deviations in table 2 do not give any evidence of this, but greater care was necessary in preparing the specimens of mortar A. Mortars B and C were, as a rule, too wet. There was a pronounded rise of water to the top of the specimens, in B more so than in C, and particularly in penetration specimens, which had to be removed from the cabinet every 30 minutes. Mortar D, which has a C/W ratio practically halfway between those of mortars A and B, seems to be the most desirable. It is estimated that for the same group of cements mortar D should give flows the average of which would be from 85 to 95 percent; and if the mortar specified be one in which the C/W ratio is controlled by flow measurements, this range would be preferable to the 100- to 110-percent range of mortar B. It is regrettable that this investigation did not include compression tests on mortars made from standard sand; for it is now realized that the so-called "graded Ottawa sand" used in this investigation is neither a graded sand nor does it produce, when used in the proportions herein studied, a truly plastic mortar which will hold water.

In specifying the particular strengths to be required it may be borne in mind that the manufacturers often claim that these cements will give, at 1 and 3 days, strengths equivalent to those attained by normal portland cements at 7 and 28 days, respectively. A comparison of the results obtained in this investigation with those obtained by Committee C–1 of the American Society for Testing Materials working on normal portland cements [5] shows that this claim of the manufacturers is hardly approached. The average compressive strengths of seven normal portland cements in plastic mortar cubes of the proportions of mortar D were 2,745 lb/in^2 and 4,655 lb/in^2 at 7 and 28 days, respectively. These values are higher, respectively, than even the maximum 1- and 3-day strengths obtained in the present investigation upon mortar A or mortar D. True, the tensile strengths of the above seven normal portland cements were far above those required by the Federal specification for portland cement, but the strengths obtained in this investigation with the standard-sand briquets show that many of the cements do not give 1- and 3-day tensile strengths equivalent to the requirements of the Federal specification for portland cement at 7 and 28 days, respectively. It seems, therefore, that to specify such strength requirements for 1 and 3 days as would be equivalent to the Federal specification requirements for normal portland cements at 7 and 28 days, respectively, would not be demanding nearly so much as manufacturers sometimes claim their product to offer and yet would reject several of the present cements and place others on the border line. If tests for tensile strength are specified, it is suggested that 275 lb/in^2 at 1 day and 375 lb/in^2 at 3 days with standard Ottawa sand briquets be the requirements; and if compressive tests are specified, it is suggested that the compressive strengths of mortar D equivalent to the above

[5] Report of working committee on plastic mortar tests for portland cement, Proc. Am. Soc. Testing Materials 21, part I, 322 (1934).

tensile strengths be the requirements. A consideration of figures 2, 3, 4, and 5 shows that approximately 1,300 lb/in^2 at 1 day and 3,000 lb/in^2 at 3 days are the compressive strengths of mortar D equivalent to tensile strengths of 275 lb/in^2 at 1 day and 375 lb/in^2 at 3 days with standard Ottawa sand briquets.

The methods followed in mixing, molding, and testing seemed satisfactory. However, the necessity of sealing the molds to the plates is questionable. This process is quite laborious and would entail considerable cost if required in a routine test. The rate of loading offers another question for economic consideration. A recent investigation at this Bureau has shown that rates of loading up to 12,000 lb/in^2 per minute gave results as reliable as those obtained when loading at 4,000 lb/in^2 per minute. The standard deviations of individual breaks were found to be practically the same at all rates of loading, and the average strengths obtained at each rate were only slightly different. It is therefore suggested that a rate of loading of from 5,000 to 6,000 lb/in^2 per minute be specified for the 3-day tests. For the 1-day tests 3,000 to 5,000 lb/in^2 per minute would be satisfactory.

The initial setting time of high-early-strength cements is a second important consideration. Early setting often accompanies early strength in these cements; therefore, especial attention should be given to adopting a means of rejecting any cement whose quick setting might present difficulties. The results in table 4 show that 5 of these cements had initial setting times of 1½ hours or less as determined with the Gillmore needle. Any method which relies on a reading of zero penetration is not sensitive. This can be seen from figures 7 and 8, which are typical of time-penetration curves on cement pastes and mortars. These curves fall off rapidly from maximum penetration and then approach zero penetration very slowly. Consequently, it is difficult to determine the precise time at which the penetration is zero, whereas the time at which the penetration is, say 35 mm, can be determined with a fair degree of precision. From the foregoing data it appears that the 300-g 2-mm needle is conveniently suited for determining the initial setting time. The 1-mm needle is undesirable because its penetrations do not begin to decrease until around 2 hours. The initial set might be defined as that stage of the mortar when the 2-mm needle will penetrate to 5 mm from the bottom of the specimen. A requirement that a cement, when incorporated in a mortar of the same proportions as mortar D, shall have an initial setting time of not less than 1 hour, would accept one or two cements in this investigation with a very narrow margin and the others with a wide margin.

Since 24-hour strength tests will be made on high-early-strength cements, it does not seem necessary to specify a final setting time.

Soundness is a third consideration in a specification for any cement. Volume changes which are not large enough to produce unsoundness in steaming at 100° C. may be undesirable, particularly in large-mass construction, and it would be advantageous to include in an acceptance specification a test upon which could be set a limit for these changes. The data obtained in this work offer little upon which to base such a specification. Until more can be learned concerning the volume changes of cement and methods for their measurement, it does not seem advisable to incorporate into a specification a test for

soundness other than the current one of steaming a pat of neat cement.

In considering a fineness requirement for these cements it is obvious that the percentage retained on a no. 200 sieve means nothing. Moreover, the customary dry method of sieving is not practicable in these cements because of the clogging. It is becoming the practice to include specific-surface requirements in cement specifications. Although the specific surface of these cements does not seem to bear any constant relation to their variations in strength, it is practically certain that much of their superiority in strength over normal portland cements is due to their finer grinding. The highest strengths were obtained with many of the cements of lowest specific surface; therefore, a requirement that the specific surface be greater than 1,900 cm^2/g would be satisfactory.

The chemical analyses of these cements showed that two cements exceeded the SO_3 content of 2.5 percent allowed in the ASTM tentative specification. In this investigation these two cements did not give evidence of any undesirable properties. Having produced no data to show otherwise, the contents of SO_3, MgO, and insoluble, and the loss on ignition allowed in the ASTM tentative specification seem to be satisfactory. Until some method can be developed for determining CaO distinct from $Ca(OH)_2$ it does not seem advisable to set a limit to the "free-lime" content.

VI. SUMMARY

1. The 28 commercial high-early-strength portland cements studied differed widely in compound composition and physical properties.

2. The calculated C_3S contents of the cements varied from 44 to 74 percent, the C_2S contents from 0 to 25 percent, and the C_3A contents from 7 to 15 percent. Two cements had SO_3 contents exceeding 2.5 percent.

3. The specific surfaces ranged from 1,990 to 2,860 cm^2/g.

4. Nine cements failed to meet the strength requirements of the ASTM Tentative Specification C 74–30T of 275 $lb/in.^2$ at 1 day, and 10 that of 375 $lb/in.^2$ at 3 days.

5. Four plastic mortars made with graded Ottawa sand were studied. Mortar A had a cement:sand ratio of 1:2.75 and a C/W ratio of 2.0 by weight. Mortar B had a cement:sand ratio of 1:2.75 and a water content adjusted to give a mortar flow of 100 to 110 percent. Mortar C had a C/W ratio of 2.0 and a sand content adjusted to give a flow of 100 to 110 percent. Mortar D had a cement:sand ratio of 1:2.77 and a C/W ratio of 1.88.

6. The flows of mortar A ranged from 59 to 105 percent. The C/W ratio of mortar B ranged from 1.72 to 2.00. The cement:sand proportions of mortar C ranged from 1:2.24 to 1:2.75.

7. The tensile strengths of mortar A ranged at 1 day from 170 to 290 $lb/in.^2$, at 3 days from 265 to 410 $lb/in.^2$, at 7 days from 320 to 455 $lb/in.^2$ and at 28 days from 390 to 420 $lb/in.^2$ The compressive strengths of mortar A ranged at 1 day from 1,030 to 2,230 $lb/in.^2$, at 3 days from 2,350 to 4,370 $lb/in.^2$, at 7 days from 3,270 to 6,300 $lb/in.^2$, and at 28 days from 4,250 to 7,100 $lb/in.^2$ The strengths of mortars C and B, as a rule, were respectively somewhat above and below those of mortar A.

8. The rate of setting was measured by the penetrations of 300-g needles, one 1 mm and one 2 mm in diameter, into the mortars contained in a Vicat ring. The 2-mm needle has been suggested as the more suitable of the two needles.

9. Six-inch prisms 1 inch square, after an initial period of 24 hours in a moist cabinet, were measured for length change under four conditions of curing. It is of note that unusual changes were obtained with the two cements having the highest "free-lime" contents.

10. The requirements for a specification for a high-early-strength cement have been discussed, and recommendations made for tests to be incorporated into such a specification.

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